

DESCRIPTION

CATALYST FOR OLEFIN POLYMERIZATION AND PROCESS FOR PRODUCING

OLEFIN POLYMER

TECHNICAL FIELD

The present invention relates to catalysts for polymerization of olefins, and to methods for producing olefinic polymers. Precisely, it relates to catalysts for olefin polymerization comprising, as one component, a specific compound, and to inexpensive and efficient methods for producing olefinic polymers with the catalysts.

BACKGROUND ART

Recently, metallocene catalysts have been developed and used for olefinic polymer production, which comprise, as the catalyst component, a transition metal compound having a π -ligand bonded to the center metal element via a group.

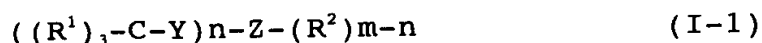
To exhibit satisfactory activity, however, the catalysts of that type require a large amount of promoters such as aluminoxanes and the like. Therefore, they are problematic in that the total catalyst costs are inevitably high, and, in addition, the catalyst residue resulting from the promoter used often remains in the polymers produced thereby unfavorably coloring the polymers.

In that situation, techniques of using clay, clay

09869331-072601

1. A catalyst for polymerization of olefins, which comprises:

- (A) a transition metal compound,
- (B) an oxygen-containing compound,
- (C) a compound of a general formula (I-1):



wherein R^1 represents an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, R^1 's may be the same or different, and R^1 's may be optionally bonded to each other to form a cyclic structure; Y represents an element of Group 16; Z represents a metal element of Groups 2 to 13; R^2 represents a hydrocarbon group; m is an integer, indicating the valency of the metal element Z; and n is an integer of from 1 to (m-1),

and optionally,

- (D) an alkylating agent.

2. The catalyst of above 1 for polymerization of olefins, wherein, in (C), Y is oxygen and Z is aluminium.

3. The catalyst of above 1 for polymerization of olefins, wherein the compound (C) is a reaction product of a compound of a general formula, $(R^1)_3-C-OR^3$, and a compound of

09869331-072601
a general formula, $Z(R^2)_m$:

in which R^1 represents an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, R^1 's may be the same or different, and R^1 's may be optionally bonded to each other to form a cyclic structure; R^3 represents a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group; Z represents a metal element of Groups 2 to 13; m is an integer, indicating the valency of the metal element Z ; and R^2 represents a hydrocarbon group.

4. A catalyst for polymerization of olefins, which comprises:

(A) a transition metal compound,

(B) an oxygen-containing compound,

(C1) a compound of a general formula, $(R^1)_3-C-OR^3$:

wherein R^1 represents an aromatic hydrocarbon group having

from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, R^1 's may be the same or different, and R^1 's may be optionally bonded to each other to form a cyclic structure; R^3 represents a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group,

(C2) a compound of a general formula, $Z(R^2)_m$, wherein Z represents a metal element of Groups 2 to 13; m is an integer, indicating the valency of the metal element Z ; and R^2 represents a hydrocarbon group,

and optionally,

(D) an alkylating agent.

5. The catalyst of any of above 1 to 4 for polymerization of olefins, wherein at least one of three R^1 's is an aromatic hydrocarbon group having from 6 to 30 carbon atoms.

6. The catalyst of any of above 1 to 4 for polymerization

THE UNIVERSITY OF CHICAGO

8. The catalyst of any of above 1 to 7 for polymerization of olefins, wherein R^2 is an alkyl group having at least 2 carbon atoms.

10. The catalyst of any of above 1 to 9 for polymerization of olefins, wherein the transition metal compound (A) is represented by any of the following general formulae (I-2) to (I-6):

$$Q_a^1(C_5H_{5-a-b}R_b^8)(C_5H_{5-a-c}R_c^9)M^1X^1Y^1 \quad (I-2)$$

$$Q^2_a(C_5H_{5-a-d}R^{10}_d)Z^1M^1X^1Y^1 \quad (I-3)$$

$$(\text{C}_5\text{H}_5\text{-eR}^{11}\text{e})\text{M}^1\text{X}^1\text{Y}^1\text{W}^1 \quad (\text{I-4})$$

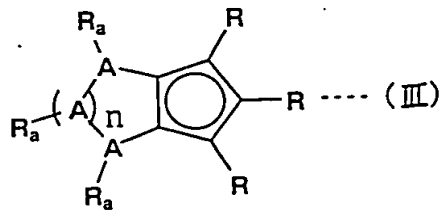
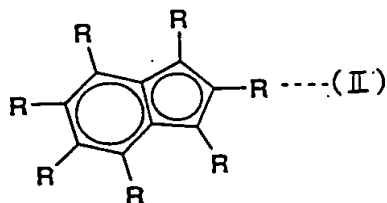
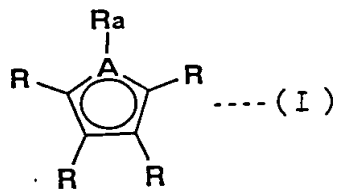
$$M^1 X^1 Y^1 W^1 U^1 \quad (I-5)$$

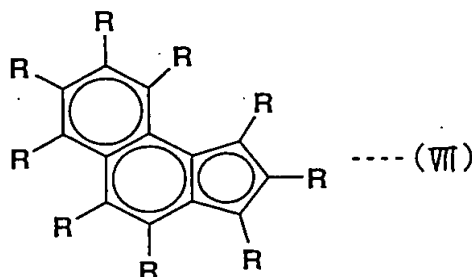
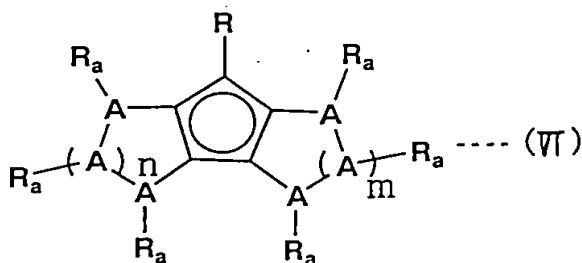
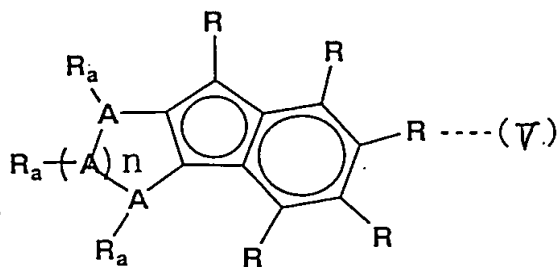
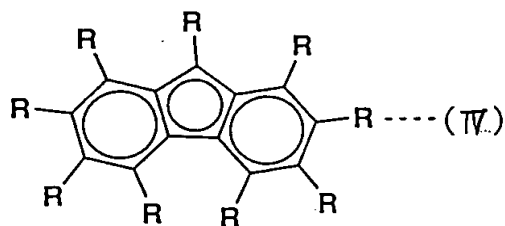
$$L^1 L^2 M^2 X^1 Y^1 \quad (I-6)$$

6

hydrocarbon group, a nitrogen-containing hydrocarbon group, or a boron-containing hydrocarbon group; and a plurality of these groups, if any, may be the same or different, and may be bonded to each other to form a cyclic structure; a represents 0, 1 or 2; b, c and d each represent an integer of from 0 to 5 when a = 0, or an integer of from 0 to 4 when a = 1, or an integer of from 0 to 3 when a = 2; e is an integer of from 0 to 5; M¹ represents a transition metal of Groups 4 to 6 of the Periodic Table; M² represents a transition metal of Groups 8 to 10 of the Periodic Table; L¹ and L² each represent a coordination-bonding ligand; X¹, Y¹, Z¹, W¹ and U¹ each represent a covalent-bonding or ionic-bonding ligand; and L¹, L², X¹, Y¹, Z¹, W¹ and U¹ may be bonded to each other to form a cyclic structure.

11. The catalyst of above 10 for polymerization of olefins, wherein, in the transition metal compound (A) of formula (I-4), the group (C₅H₅...R¹¹...) is represented by any of the following general formulae (I) to (VII):





wherein A represents an element of Group 13, 14, 15 or 16, and plural A's may be the same or different; R represents a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, a carboxyl group, or an alkylsilyl or alkylsilylalkyl group having from 3 to 30 carbon atoms, and R's may be the same or different, and may be optionally bonded to each other to form a cyclic structure; a represents 0, 1 or 2; and n

and m each represent an integer of at least 1.

12. A method for producing olefinic polymers, which comprises polymerizing olefins in the presence of the polymerization catalyst of any of above 1 to 11.

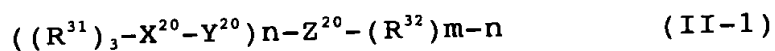
Another aspect of the invention is to provide a catalyst for polymerization of olefins and a method for producing olefinic polymers, which are as follows:

1. A catalyst for polymerization of olefins, which comprises:

(A) a transition metal compound,

(B) a compound capable of reacting with a transition metal compound to form an ionic complex,

(C) a compound of a general formula (II-1):



wherein R^{31} represents a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, R^{31} 's may be the same or different, and R^{31} 's may be optionally bonded to each other to form a cyclic structure; X^{20} represents an element of Group 14; Y^{20} represents an element of Group

16; Z^{20} represents a metal element of Groups 2 to 13; R^{32} represents a hydrocarbon group; m is an integer, indicating the valency of the metal element Z^{20} ; and n is an integer of from 1 to $(m-1)$,

and optionally,

(D) an alkylating agent.

2. The catalyst of above 1 for polymerization of olefins, wherein, in (C), Y^{20} is oxygen and Z^{20} is aluminium.

3. The catalyst of above 1 for polymerization of olefins, wherein the compound (C) is a reaction product of a compound of a general formula, $(R^{31})_3-C-OR^{33}$, and a compound of a general formula, $Z^{20}(R^{32})_m$:

in which R^{31} represents a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, R^{31} 's may be the same or different, and R^{31} 's may be optionally bonded to each other to form a cyclic structure; Z^{20} represents a metal element of Groups 2 to 13; R^{32} represents a hydrocarbon group; R^{33} represents a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30

carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, and may be the same or different; m is an integer, indicating the valency of the metal element Z^{20} ; and n is an integer of from 1 to (m-1).

4. A catalyst for polymerization of olefins, which comprises:

(A) a transition metal compound,

(B) a compound capable of reacting with a transition metal compound to form an ionic complex,

(C1) a compound of a general formula, $(R^{31})_3-C-OR^{33}$:

wherein R^{31} represents a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, R^{31} 's may be the same or different, and R^{31} 's may be optionally bonded to each other to form a cyclic structure; R^{33} represents

09869331-072601
TOP SECRET
a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, and may be the same or different,

(C2) a compound of a general formula, $Z^{20}(R^{32})_m$, wherein Z^{20} represents a metal element of Groups 2 to 13; m is an integer, indicating the valency of the metal element Z^{20} ; and R^{32} represents a hydrocarbon group,

and optionally,

(D) an alkylating agent.

5. The catalyst of any of above 1 to 4 for polymerization of olefins, wherein at least one of three R^{31} 's is an aromatic hydrocarbon group having from 6 to 30 carbon atoms.

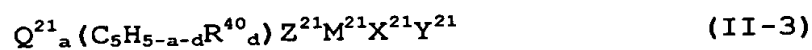
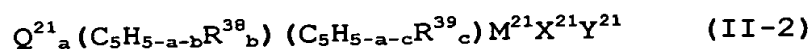
6. The catalyst of any of above 1 to 4 for polymerization of olefins, wherein three R^{31} 's are all aromatic hydrocarbon groups each having from 6 to 30 carbon atoms.

7. The catalyst of any of above 1 to 4 for polymerization of olefins, wherein three R^{31} 's are all phenyl groups.

8. The catalyst of any of above 1 to 7 for polymerization of olefins, wherein R^{32} is an alkyl group having at least 2 carbon atoms.

9. The catalyst of any of above 3 to 8 for polymerization of olefins, wherein Z is aluminium.

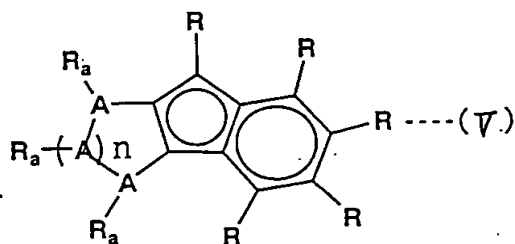
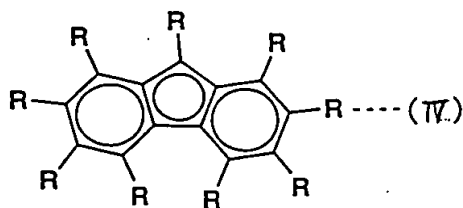
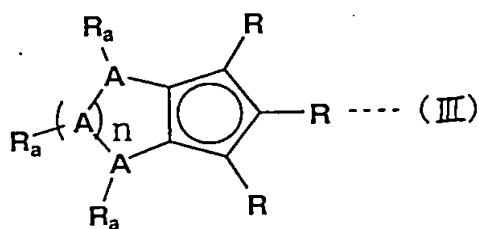
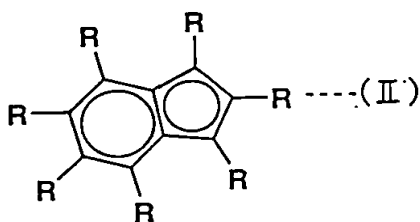
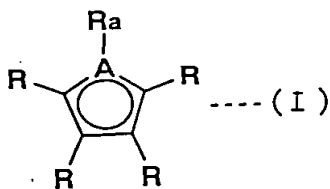
10. The catalyst of any of above 1 to 9 for polymerization of olefins, wherein the transition metal compound (A) is represented by any of the following general formulae (II-2) to (II-6):

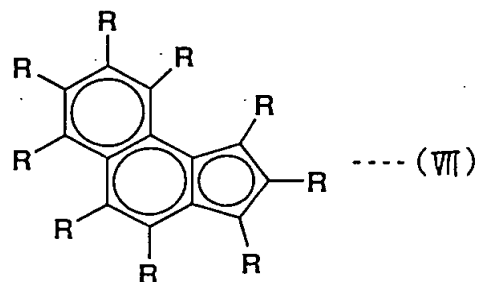
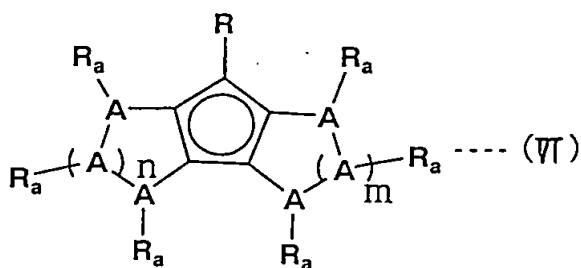


in which Q^{21} represents a bonding group that crosslinks the two conjugated five-membered cyclic ligands $(C_5H_{5-a-b}R^{38}_b)$ and $(C_5H_{5-a-c}R^{39}_c)$; Q^{22} represents a bonding group that crosslinks the conjugated five-membered cyclic ligand $(C_5H_{5-a-d}R^{40}_d)$ and the group Z^{21} ; R^{38} , R^{39} , R^{40} and R^{41} each represent a hydrocarbon group, a halogen atom, an alkoxy group, a silicon-containing hydrocarbon group, a phosphorus-containing hydrocarbon group, a nitrogen-containing hydrocarbon group, or a boron-containing hydrocarbon group; and a plurality of these groups, if any, may be the same or different, and may be bonded to each other to form a cyclic structure; a represents 0, 1 or 2; b, c and d each represent an integer of from 0 to 5 when a = 0, or an integer of from 0 to 4 when a = 1, or an integer of

from 0 to 3 when $a = 2$; e is an integer of from 0 to 5; M^{21} represents a transition metal of Groups 4 to 6 of the Periodic Table; M^{22} represents a transition metal of Groups 8 to 10 of the Periodic Table; L^{21} and L^{22} each represent a coordination-bonding ligand; X^{21} , Y^{21} , Z^{21} , W^{21} and U^{21} each represent a covalent-bonding or ionic-bonding ligand; and L^{21} , L^{22} , X^{21} , Y^{21} , Z^{21} , W^{21} and U^{21} may be bonded to each other to form a cyclic structure.

11. The catalyst of above 10 for polymerization of olefins, wherein, in the transition metal compound (A) of formula (II-4), the group $(C_5H_5-eR^{41})_e$ is represented by any of the following general formulae (I) to (VII):





wherein A represents an element of Group 13, 14, 15 or 16, and plural A's may be the same or different; R represents a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, a carboxyl group, or an alkylsilyl or alkylsilylalkyl group having from 3 to 30 carbon atoms, and R's may be the same or different, and may be optionally bonded to each other to form a cyclic structure; a represents 0, 1 or 2; and n and m each represent an integer of at least 1.

12. A method for producing olefinic polymers, which comprises polymerizing olefins in the presence of the polymerization catalyst of any of above 1 to 11.

BEST MODES OF CARRYING OUT THE INVENTION

The first and second aspects of the invention are

described below with reference to their embodiments.

[First aspect of the invention]

In this section, the first aspect of the invention will be simply referred to as "the invention".

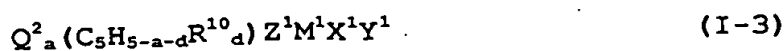
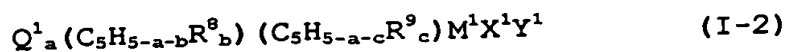
I. Catalyst for polymerization of olefins:

1. Components of catalyst for polymerization of olefins:

The catalyst of the invention for polymerization of olefins comprises (A) a transition metal compound, (B) an oxygen-containing compound, and (C) a compound of formula (I) which will be described in detail hereinafter, and optionally (D) an alkylating agent. The constituent components are described below.

(1) (A) Transition metal compound:

Various types of transition metal compounds are usable as the component (A) in the invention, but preferred are transition metal compounds of Groups 4 to 6 of the Periodic Table, or transition metal compounds of Groups 8 to 10 thereof. As the transition metal compounds of Groups 4 to 6 of the Periodic Table, preferred are those of the following general formulae (I-2) to (I-5). As the transition metal compounds of Groups 8 to 10 of the Periodic Table, preferred are those of the following general formula (I-6).





wherein Q^1 represents a bonding group that crosslinks the two conjugated five-membered cyclic ligands ($C_5H_{5-a-b}R^8_b$) and ($C_5H_{5-a-c}R^9_c$); Q^2 represents a bonding group that crosslinks the conjugated five-membered cyclic ligand ($C_5H_{5-a-d}R^{10}_d$) and the group Z^1 ; R^8 , R^9 , R^{10} and R^{11} each represent a hydrocarbon group, a halogen atom, an alkoxy group, a silicon-containing hydrocarbon group, a phosphorus-containing hydrocarbon group, a nitrogen-containing hydrocarbon group, or a boron-containing hydrocarbon group; and a plurality of these groups, if any, may be the same or different, and may be bonded to each other to form a cyclic structure; a represents 0, 1 or 2; b, c and d each represent an integer of from 0 to 5 when a = 0, or an integer of from 0 to 4 when a = 1, or an integer of from 0 to 3 when a = 2; e is an integer of from 0 to 5; M^1 represents a transition metal of Groups 4 to 6 of the Periodic Table; M^2 represents a transition metal of Groups 8 to 10 of the Periodic Table; L^1 and L^2 each represent a coordination-bonding ligand; X^1 , Y^1 , Z^1 , W^1 and U^1 each represent a covalent-bonding or ionic-bonding ligand; and L^1 , L^2 , X^1 , Y^1 , Z^1 , W^1 and U^1 may be bonded to each other to form a cyclic structure.

Specific examples of Q^1 and Q^2 in formulae (I-2) and (I-3) include (1) an alkylene group having from 1 to 4 carbon atoms, or a cycloalkylene group, or the group substituted by

09869331-072601

a lower alkyl or phenyl group at its side chain, such as a methylene group, an ethylene group, an isopropylene group, a methylphenylmethylene group, a diphenylmethylene group, a cyclohexylene group, etc.; (2) a silylene group, or an oligosilylene group, or the group substituted by a lower alkyl or phenyl group at its side chain, such as a silylene group, a dimethylsilylene group, a methylphenylsilylene group, a diphenylsilylene group, a disilylene group, a tetramethyldisilylene group, etc.; and (3) a hydrocarbon group (e.g., a lower alkyl group, a phenyl group, a hydrocarbyloxy group (preferably, a lower alkoxy group), etc.) containing germanium, phosphorus, nitrogen, boron or aluminium, such as a $(\text{CH}_3)_2\text{Ge}$ group, a $(\text{C}_6\text{H}_5)_2\text{Ge}$ group, a $(\text{CH}_3)\text{P}$ group, a $(\text{C}_6\text{H}_5)\text{P}$ group, a $(\text{C}_4\text{H}_9)\text{N}$ group, a $(\text{C}_6\text{H}_5)\text{N}$ group, a $(\text{CH}_3)\text{B}$ group, a $(\text{C}_4\text{H}_9)\text{B}$ group, a $(\text{C}_6\text{H}_5)\text{B}$ group, a $(\text{C}_6\text{H}_5)\text{Al}$ group, a $(\text{CH}_3\text{O})\text{Al}$ group, etc. Of those, preferred are alkylene groups and silylene groups.

$(\text{C}_5\text{H}_5\text{-a-bR}^8\text{b})$, $(\text{C}_5\text{H}_5\text{-a-cR}^9\text{c})$ and $(\text{C}_5\text{H}_5\text{-a-dR}^{10}\text{d})$ are conjugated, 5-membered cyclic ligands, in which R^8 , R^9 and R^{10} each represent a hydrocarbon group, a halogen atom, an alkoxy group, a silicon-containing hydrocarbon group, a phosphorus-containing hydrocarbon group, a nitrogen-containing hydrocarbon group, or a boron-containing hydrocarbon group; a represents 0, 1 or 2; and b, c and d each represent an integer of from 0 to 5 when a = 0, or an integer

of from 0 to 4 when $a = 1$, or an integer of from 0 to 3 when $a = 2$. The hydrocarbon group preferably has from 1 to 20 carbon atoms, more preferably from 1 to 12 carbon atoms. The hydrocarbon group may be a monovalent one that bonds to the cyclopentadienyl group of a conjugated, 5-membered cyclic group. Two of plural hydrocarbon groups, if any, may be bonded to each other to form a cyclic structure along with a part of the cyclopentadienyl group. Specific examples of those conjugated, 5-membered cyclic ligands are substituted or unsubstituted cyclopentadienyl groups, indenyl groups and fluorenyl groups. The halogen atom includes chlorine, bromine, iodine and fluorine atoms. The alkoxy group preferably has from 1 to 12 carbon atoms. The silicon-containing hydrocarbon group includes, for example, groups of $-\text{Si}(\text{R}^{12})(\text{R}^{13})(\text{R}^{14})$, in which R^{12} , R^{13} and R^{14} each represent a hydrocarbon group having from 1 to 24 carbon atoms. As the phosphorus-containing hydrocarbon group, the nitrogen-containing hydrocarbon group and the boron-containing hydrocarbon group, for example, mentioned are groups of $-\text{P}(\text{R}^{15})(\text{R}^{16})$, $-\text{N}(\text{R}^{15})(\text{R}^{16})$, and $-\text{B}(\text{R}^{15})(\text{R}^{16})$, respectively, in which R^{15} and R^{16} each represent a hydrocarbon group having from 1 to 18 carbon atoms. Plural R^8 's, R^9 's and R^{10} 's, if any, may be the same or different ones, respectively. In formula (I-2), the conjugated, 5-membered cyclic ligands $(\text{C}_5\text{H}_5\text{-a-bR}^8_b)$ and $(\text{C}_5\text{H}_5\text{-a-cR}^9_c)$ may be the same or different ones.

09869331-072601

M¹ represents a transition metal element of Groups 4 to 6 of the Periodic Table, including, for example, titanium, zirconium, hafnium, niobium, molybdenum, tungsten, etc. Of those, preferred are titanium, zirconium and hafnium, and more preferred is zirconium. Z¹ represents a covalent-bonding ligand, including, for example, oxygen (-O-), sulfur (-S-), an alkoxy group having from 1 to 20, preferably from 1 to 10 carbon atoms, a thioalkoxy group having from 1 to 20, preferably from 1 to 12 carbon atoms, a nitrogen-containing hydrocarbon group having from 1 to 40, preferably from 1 to 18 carbon atoms, and a phosphorus-containing hydrocarbon group having from 1 to 40, preferably from 1 to 18 carbon atoms. X¹ and Y¹ each represent a covalent-bonding ligand, including, for example, a hydrogen atom, a halogen atom, a hydrocarbon group having from 1 to 20, preferably from 1 to 10 carbon atoms, an alkoxy group having from 1 to 20, preferably from 1 to 10 carbon atoms, an amino group, a phosphorus-containing hydrocarbon group having from 1 to 20, preferably from 1 to 12 carbon atoms (e.g., a diphenylphosphine group, etc.), a silicon-containing hydrocarbon group having from 1 to 20, preferably from 1 to 12 carbon atoms (e.g., a trimethylsilyl group, etc.), and a boron compound residue having a hydrocarbon group with from 1 to 20, preferably from 1 to 12 carbon atoms or having halogens (e.g., B(C₆H₅)₄, BF₄). Of those, preferred are halogen atoms

and hydrocarbon groups. X^1 and Y^1 may be the same or different, and they may be bonded to each other to form a cyclic structure.

In formula (I-4), M^1 represents a transition metal of Groups 4 to 6 of the Periodic Table, such as that mentioned above; and X^1 and Y^1 have the same meanings as above. The meanings of X^1 and Y^1 shall apply to W^1 . Namely, W^1 is a covalent-bonding ligand, including, for example, a hydrogen atom, a halogen atom, a hydrocarbon group having from 1 to 20, preferably from 1 to 10 carbon atoms, an alkoxy group having from 1 to 20, preferably from 1 to 10 carbon atoms, an amino group, a phosphorus-containing hydrocarbon group having from 1 to 20, preferably from 1 to 12 carbon atoms (e.g., a diphenylphosphine group, etc.), a silicon-containing hydrocarbon group having from 1 to 20, preferably from 1 to 12 carbon atoms (e.g., a trimethylsilyl group, etc.), and a boron compound residue having a hydrocarbon group with from 1 to 20, preferably from 1 to 12 carbon atoms or having halogens (e.g., $B(C_6H_5)_4$, BF_4). Of those, preferred are halogen atoms and hydrocarbon groups. X^1 , Y^1 and W^1 may be the same or different, and they may be bonded to each other to form a cyclic structure.

In formula (I-5), M^1 represents a transition metal of Groups 4 to 6 of the Periodic Table, such as that mentioned above; and X^1 , Y^1 and W^1 have the same meanings as above. The meanings of X^1 , Y^1 and W^1 shall apply to U^1 . Namely, U^1 is a

covalent-bonding ligand, including, for example, a hydrogen atom, a halogen atom, a hydrocarbon group having from 1 to 20, preferably from 1 to 10 carbon atoms, an alkoxy group having from 1 to 20, preferably from 1 to 10 carbon atoms, an amino group, a phosphorus-containing hydrocarbon group having from 1 to 20, preferably from 1 to 12 carbon atoms (e.g., a diphenylphosphine group, etc.), a silicon-containing hydrocarbon group having from 1 to 20, preferably from 1 to 12 carbon atoms (e.g., a trimethylsilyl group, etc.), and a boron compound residue having a hydrocarbon group with from 1 to 20, preferably from 1 to 12 carbon atoms or having halogens (e.g., $B(C_6H_5)_4$, BF_4). Of those, preferred are halogen atoms and hydrocarbon groups. x^1 , y^1 , w^1 and u^1 may be the same or different, and they may be bonded to each other to form a cyclic structure.

(I) As specific examples of the transition metal compounds of formulae (I-2) and (I-3), mentioned are the following compounds. In the compounds to be mentioned below, titanium may be replaced with zirconium, and such zirconium compounds are also referred to herein to the same effect.

(1) Transition metal compounds not having a crosslinkable bonding group but having two conjugated, 5-membered cyclic ligands, such as

| | |
|-------------------------------------|-------------|
| bis(cyclopentadienyl)titanium | dichloride, |
| bis(methylcyclopentadienyl)titanium | dichloride, |

bis(dimethylcyclopentadienyl)titanium dichloride,
 bis(trimethylcyclopentadienyl)titanium dichloride,
 bis(tetramethylcyclopentadienyl)titanium dichloride,
 bis(pentamethylcyclopentadienyl)titanium dichloride,
 bis(n-butylcyclopentadienyl)titanium dichloride,
 bis(indenyl)titanium dichloride, bis(fluorenyl)titanium
 dichloride, bis(cyclopentadienyl)titanium chlorohydride,
 bis(cyclopentadienyl)methyltitanium chloride,
 bis(cyclopentadienyl)ethyltitanium chloride,
 bis(cyclopentadienyl)phenyltitanium chloride,
 bis(cyclopentadienyl)dimethyltitanium,
 bis(cyclopentadienyl)diphenyltitanium,
 bis(cyclopentadienyl)dineopentyltitanium,
 bis(cyclopentadienyl)dihydrotitanium,
 (cyclopentadienyl)(indenyl)titanium dichloride,
 (cyclopentadienyl)(fluorenyl)titanium dichloride, etc.

(2) Transition metal compounds having two conjugated,
 5-membered cyclic ligands, in which the two ligands are
 crosslinked with an alkylene group, such as
 methylenebis(indenyl)titanium dichloride,
 ethylenebis(indenyl)titanium dichloride,
 methylenebis(indenyl)titanium chlorohydride,
 ethylenebis(indenyl)methyltitanium chloride,
 ethylenebis(indenyl)methoxychlorotitanium,
 ethylenebis(indenyl)titanium diethoxide,

ethylenebis(indenyl)dimethyltitanium, ethylenebis(4,5,6,7-tetrahydroindenyl)titanium dichloride, ethylenebis(2-methylindenyl)titanium dichloride, ethylenebis(2,4-dimethylindenyl)titanium dichloride, ethylenebis(2-methyl-4-trimethylsilylindenyl)titanium dichloride, ethylenebis(2,4-dimethyl-5,6,7-trihydroindenyl)titanium dichloride, ethylene(2,4-dimethylcyclopentadienyl)(3',5'-dimethylcyclopentadienyl)titanium dichloride, ethylene(2-methyl-4-t-butylcyclopentadienyl)(3'-t-butyl-5'-methylcyclopentadienyl)titanium dichloride, ethylene(2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl)titanium dichloride, isopropylidenebis(2-methylindenyl)titanium dichloride, isopropylidenebis(indenyl)titanium dichloride, isopropylidenebis(2,4-dimethylindenyl)titanium dichloride, isopropylidene(2,4-dimethylcyclopentadienyl)(3',5'-dimethylcyclopentadienyl)titanium dichloride, isopropylidene(2-methyl-4-t-butylcyclopentadienyl)(3'-t-butyl-5'-methylcyclopentadienyl)titanium dichloride, methylene(cyclopentadienyl)(3,4-dimethylcyclopentadienyl)titanium dichloride, methylene(cyclopentadienyl)(3,4-dimethylcyclopentadienyl)titanium chlorohydrate, methylene(cyclopentadienyl)(3,4-dimethylcyclopentadienyl)dimethyltitanium,

diethylcyclopentadienyl)titanium dichloride,
 diphenylmethylenecyclopentadienyl)(3,4-
 diethylcyclopentadienyl)titanium dichloride,
 cyclohexylidene(cyclopentadienyl)(fluorenyl)titanium
 dichloride, cyclohexylidene(2,5-
 dimethylcyclopentadienyl)(3',4'-
 dimethylcyclopentadienyl)titanium dichloride, etc.

(3) Transition metal compounds having two silylene-
 crosslinked, conjugated, 5-membered cyclic ligands, such as
 dimethylsilylenebis(indenyl)titanium dichloride,
 dimethylsilylenebis(4,5,6,7-tetrahydroindenyl)titanium
 dichloride, dimethylsilylenebis(2-methylindenyl)titanium
 dichloride, dimethylsilylenebis(2,4-
 dimethylindenyl)titanium dichloride,
 dimethylsilylenebis(2,4-dimethylcyclopentadienyl)(3',5'-
 dimethylcyclopentadienyl)titanium dichloride,
 phenylmethylsilylenebis(indenyl)titanium dichloride,
 phenylmethylsilylenebis(4,5,6,7-tetrahydroindenyl)titanium
 dichloride, phenylmethylsilylenebis(2,4-
 dimethylindenyl)titanium dichloride,
 phenylmethylsilylene(2,4-dimethylcyclopentadienyl)(3',5'-
 dimethylcyclopentadienyl)titanium dichloride,
 phenylmethylsilylene(2,3,5-
 trimethylcyclopentadienyl)(2',4',5'-
 trimethylcyclopentadienyl)titanium dichloride,

phenylmethylsilylenebis(tetramethylcyclopentadienyl)-
 titanium dichloride, diphenylsilylenebis(2,4-
 dimethylindenyl)titanium dichloride,
 diphenylsilylenebis(indenyl)titanium dichloride,
 diphenylsilylenebis(2-methylindenyl)titanium dichloride,
 tetramethyldisilylenebis(indenyl)titanium dichloride,
 tetramethyldisilylenebis(cyclopentadienyl)titanium
 dichloride, tetramethyldisilylene(3-
 methylcyclopentadienyl)(indenyl)titanium dichloride,
 dimethylsilylene(cyclopentadienyl)(3,4-
 dimethylcyclopentadienyl)titanium dichloride,
 dimethylsilylene-
 (cyclopentadienyl)(trimethylcyclopentadienyl)titanium
 dichloride, dimethylsilylene-
 (cyclopentadienyl)(tetramethylcyclopentadienyl)titanium
 dichloride, dimethylsilylene(cyclopentadienyl)(3,4-
 diethylcyclopentadienyl)titanium dichloride,
 dimethylsilylene-
 (cyclopentadienyl)(triethylcyclopentadienyl)titanium
 dichloride, dimethylsilylene-
 (cyclopentadienyl)(tetraethylcyclopentadienyl)titanium
 dichloride,
 dimethylsilylene(cyclopentadienyl)(fluorenyl)titanium
 dichloride, dimethylsilylene(cyclopentadienyl)(2,7-di-t-
 butylfluorenyl)titanium dichloride, dimethylsilylene-

(cyclopentadienyl)(octahydrofluorenyl)titanium dichloride,
 dimethylsilylene(2-
 methylcyclopentadienyl)(fluorenyl)titanium dichloride,
 dimethylsilylene(2,5-
 dimethylcyclopentadienyl)(fluorenyl)titanium dichloride,
 dimethylsilylene(2-
 ethylcyclopentadienyl)(fluorenyl)titanium dichloride,
 dimethylsilylene(2,5-
 diethylcyclopentadienyl)(fluorenyl)titanium dichloride,
 diethylsilylene(2-methylcyclopentadienyl)(2',7'-di-t-
 butylfluorenyl)titanium dichloride, dimethylsilylene(2,5-
 dimethylcyclopentadienyl)(2',7'-di-t-
 butylfluorenyl)titanium dichloride, dimethylsilylene(2-
 ethylcyclopentadienyl)(2',7'-di-t-butylfluorenyl)titanium
 dichloride, dimethylsilylene(diethylcyclopentadienyl)(2,7-
 di-t-butylfluorenyl)titanium dichloride, dimethylsilylene-
 (methylcyclopentadienyl)(octahydrofluorenyl)titanium
 dichloride, dimethylsilylene-
 (dimethylcyclopentadienyl)(octahydrofluorenyl)titanium
 dichloride, dimethylsilylene-
 (ethylcyclopentadienyl)(octahydrofluorenyl)titanium
 dichloride, dimethylsilylene-
 (diethylcyclopentadienyl)(octahydrofluorenyl)titanium
 dichloride, etc.

dichloride, dimethylsilylene(tetrahydroindenyl)-
 [bis(trimethylsilyl)amino]titanium dichloride,
 dimethylgermylene-
 (tetramethylcyclopentadienyl)phenylaminotitanium
 dichloride, pentamethylcyclopentadienyltitanium
 trimethoxide, pentamethylcyclopentadienyltitanium
 trichloride, (t-butylamido)(tetramethyl- η^5 -
 cyclopentadienyl)silane-titaniumdimethyl, (t-
 butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethane-
 diyltitanium dichloride, (methylamido)(tetramethyl- η^5 -
 cyclopentadienyl)-1,2-ethane-diyltitanium dichloride,
 (ethylamido)(tetramethyl- η^5 -cyclopentadienyl)-
 methylenetitanium dichloride, (t-butylamido)dimethyl-
 (tetramethyl- η^5 -cyclopentadienyl)silane-titanium dichloride,
 (benzylamido)dimethyl-(tetramethyl- η^5 -
 cyclopentadienyl)silane-titanium dichloride,
 (phenylphosphido)dimethyl-(tetramethyl- η^5 -
 cyclopentadienyl)silane-titaniumdibenzyl, etc.

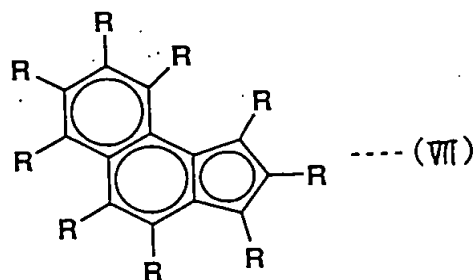
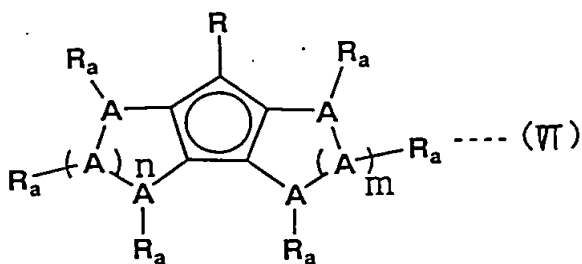
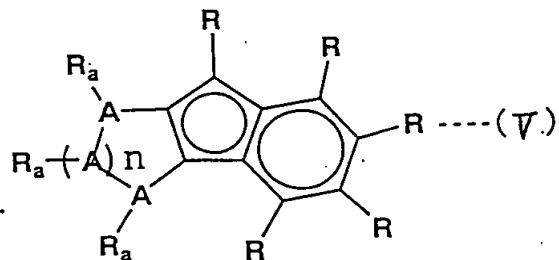
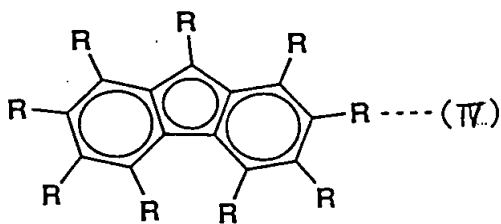
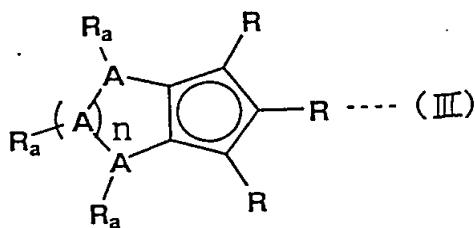
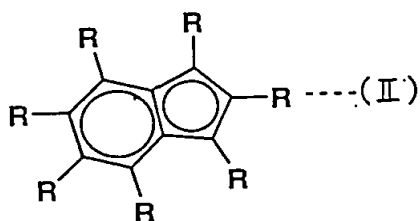
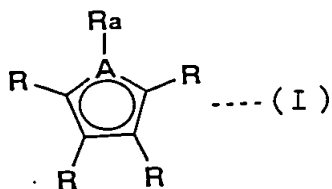
(6) Transition metal compounds having two conjugated,
 5-membered cyclic ligands in which the ligands are double-
 crosslinked, such as (1,1'-dimethylsilylene)(2,2'-
 isopropylene)bis(cyclopentadienyl)titanium dichloride,
 (1,1'-dimethylsilylene)(2,2'-dimethylsilylene)-
 bis(cyclopentadienyl)titanium dichloride, (1,1'-
 dimethylsilylene)(2,2'-isopropylidene)-

bis(cyclopentadienyl)dimethyltitanium, (1,1'-
 dimethylsilylene) (2,2'-isopropylidene) -
 bis(cyclopentadienyl)dibenzyltitanium, (1,1'-
 dimethylsilylene) (2,2'-isopropylidene) -
 bis(cyclopentadienyl)bis(trimethylsilyl)titanium, (1,1'-
 dimethylsilylene) (2,2'-isopropylidene) -
 bis(cyclopentadienyl)bis(trimethylsilylmethyl)titanium,
 (1,2'-dimethylsilylene) (2,1'-ethylene) -
 bis(indenyl)titanium dichloride, (1,1'-
 dimethylsilylene) (2,2'-ethylene) -bis(indenyl)titanium
 dichloride, (1,1'-ethylene) (2,2'-dimethylsilylene) -
 bis(indenyl)titanium dichloride, (1,1'-
 dimethylsilylene) (2,2'-cyclohexylidene) -
 bis(indenyl)titanium dichloride, etc.

(7) Derivatives from compounds of (1) to (6) noted
 above, which are produced by substituting the chlorine atoms
 in those compounds of (1) to (6) with any of a bromine atom,
 an iodine atom, a hydrogen atom, a methyl group, a phenyl group
 and others, and by substituting the center metal, titanium in
 those transition metal compounds with any of zirconium, hafnium,
 niobium, molybdenum, tungsten and others.

(II) As specific examples of the transition metal
 compounds of formula (I-4), mentioned are the following
 compounds.

They are transition metal compounds of formula (I-4),
in which the group $(C_5H_5-R^{11})$ is any of the following formulae
(I) to (VII):

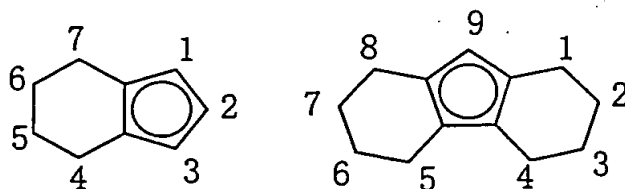


00000331-072601

wherein A represents an element of Group 13, 14, 15 or 16, and plural A's may be the same or different; R represents a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, a carboxyl group, or an alkylsilyl or alkylsilylalkyl group having from 3 to 30 carbon atoms, and R's may be the same or different, and may be optionally bonded to each other to form a cyclic structure; a represents 0, 1 or 2; and n and m each represent an integer of at least 1.

Specific examples of the group $(C_5H_5 \cdots R^{11})$ are mentioned below.

In the indenyl derivatives and the fluorenyl derivatives, the position of each substituent is indicated by the following position numbers.



The group $(C_5H_5 \cdots R^{11})$ includes, for example, a cyclopentadienyl group, a methylcyclopentadienyl group, a

group, a 1-ethyl-2-methyl-4,5,6,7-tetrahydroindenyl group, a 1-ethyl-3-methyl-4,5,6,7-tetrahydroindenyl group, a 1-ethyl-2,3-dimethyl-4,5,6,7-tetrahydroindenyl group, a 1,2-diethyl-4,5,6,7-tetrahydroindenyl group, a 1,2-diethyl-3-methyl-4,5,6,7-tetrahydroindenyl group, a 1,3-diethyl-4,5,6,7-tetrahydroindenyl group, a 1,3-diethyl-2-methyl-4,5,6,7-tetrahydroindenyl group, a 1,2,3-triethyl-4,5,6,7-tetrahydroindenyl group, a 2-ethyl-4,5,6,7-tetrahydroindenyl group, a 1-methyl-2-ethyl-4,5,6,7-tetrahydroindenyl group, a 1,3-dimethyl-2-ethyl-4,5,6,7-tetrahydroindenyl group, a fluorenyl group, a 9-methylfluorenyl group, a 9-ethylfluorenyl group, a 1,2,3,4-tetrahydrofluorenyl group, a 9-methyl-1,2,3,4-tetrahydrofluorenyl group, a 9-ethyl-1,2,3,4-tetrahydrofluorenyl group, a 1,2,3,4,5,6,7,8-octahydrofluorenyl group, a 9-methyl-1,2,3,4,5,6,7,8-octahydrofluorenyl group, a 9-ethyl-1,2,3,4,5,6,7,8-octahydrofluorenyl group, etc.

Specific examples of the transition metal compounds of formula (I-4) are mentioned below. In these, titanium may be replaced with zirconium, and such zirconium compounds are also referred to herein to the same effect.

| | | |
|---|---------------|------------------------------|
| methylcyclopentadienyltitaniumtrimethyl, | | |
| methylcyclopentadienyltitanium | trimethoxide, | |
| methylcyclopentadienyltitaniumtribenzyl, | | |
| dimethylcyclopentadienyltitanium | trichloride, | |
| dimethylcyclopentadienyltitaniumtrimethyl, | | |
| dimethylcyclopentadienyltitanium | trimethoxide, | |
| dimethylcyclopentadienyltitaniumtribenzyl, | | |
| trimethylcyclopentadienyltitanium | trichloride, | |
| trimethylcyclopentadienyltitaniumtrimethyl, | | |
| trimethylcyclopentadienyltitanium | trimethoxide, | |
| trimethylcyclopentadienyltitaniumtribenzyl, | | |
| tetramethylcyclopentadienyltitanium | trichloride, | |
| tetramethylcyclopentadienyltitaniumtrimethyl, | | |
| tetramethylcyclopentadienyltitanium | trimethoxide, | |
| tetramethylcyclopentadienyltitaniumtribenzyl, | | |
| pentamethylcyclopentadienyltitanium | trichloride, | |
| pentamethylcyclopentadienyltitaniumtrimethyl, | | |
| pentamethylcyclopentadienyltitanium | trimethoxide, | |
| pentamethylcyclopentadienyltitaniumtribenzyl, | | |
| indenyltitanium | trichloride, | indenyltitaniumtrimethyl, |
| indenyltitanium | trimethoxide, | indenyltitaniumtribenzyl, 1- |
| methylinde | trichloride, | 1- |
| methylinde | 1-methylinde | |
| trimethoxide, | 1-methylinde | 2- |
| methylinde | trichloride, | 2- |

| | | | | |
|-----------------|--------------|---------------|--------------|-------------------|
| methylinde | nyltitanium | trimethyl, | 2-methylinde | nyltitanium |
| trimethoxide, | 1-methylinde | nyltitanium | tribenzyl, | 1,2- |
| dimethylinde | nyltitanium | trichloride, | | 1,2- |
| dimethylinde | nyltitanium | trimethyl, | | 1,2- |
| dimethylinde | nyltitanium | trimethoxide, | | 1,2- |
| dimethylinde | nyltitanium | tribenzyl, | | 1,3- |
| dimethylinde | nyltitanium | trichloride, | | 1,3- |
| dimethylinde | nyltitanium | trimethyl, | | 1,3- |
| dimethylinde | nyltitanium | trimethoxide, | | 1,3- |
| dimethylinde | nyltitanium | tribenzyl, | | 1,2,3- |
| trimethylinde | nyltitanium | trichloride, | | 1,2,3- |
| trimethylinde | nyltitanium | trimethyl, | | 1,2,3- |
| trimethylinde | nyltitanium | trimethoxide, | | 1,2,3- |
| trimethylinde | nyltitanium | tribenzyl, | | 1,2,3,4,5,6,7- |
| heptamethylinde | nyltitanium | trichloride, | | 1,2,3,4,5,6,7- |
| heptamethylinde | nyltitanium | trimethyl, | | 1,2,3,4,5,6,7- |
| heptamethylinde | nyltitanium | trimethoxide, | | 1,2,3,4,5,6,7- |
| heptamethylinde | nyltitanium | tribenzyl, | | 4,5,6,7- |
| tetrahydroinde | nyltitanium | trichloride, | | 4,5,6,7- |
| tetrahydroinde | nyltitanium | trimethyl, | | 4,5,6,7- |
| tetrahydroinde | nyltitanium | trimethoxide, | | 4,5,6,7- |
| tetrahydroinde | nyltitanium | tribenzyl, | | 1-methyl-4,5,6,7- |
| tetrahydroinde | nyltitanium | trichloride, | | 1-methyl-4,5,6,7- |
| tetrahydroinde | nyltitanium | trimethyl, | | 1-methyl-4,5,6,7- |
| tetrahydroinde | nyltitanium | trimethoxide, | | 1-methyl-4,5,6,7- |

tetrahydroindenyltitaniumtribenzyl, 2-methyl-4,5,6,7-
tetrahydroindenyltitanium trichloride, 2-methyl-4,5,6,7-
tetrahydroindenyltitanium trimethoxide, 2-methyl-4,5,6,7-
tetrahydroindenyltitaniumtribenzyl, 1,2-dimethyl-4,5,6,7-
tetrahydroindenyltitanium trichloride, 1,2-dimethyl-
4,5,6,7-tetrahydroindenyltitaniumtrimethyl, 1,2-dimethyl-
4,5,6,7-tetrahydroindenyltitanium trimethoxide, 1,2-
dimethyl-4,5,6,7-tetrahydroindenyltitaniumtribenzyl, 1,3-
dimethyl-4,5,6,7-tetrahydroindenyltitanium trichloride,
1,3-dimethyl-4,5,6,7-tetrahydroindenyltitaniumtrimethyl,
1,3-dimethyl-4,5,6,7-tetrahydroindenyltitanium
trimethoxide, 1,3-dimethyl-4,5,6,7-
tetrahydroindenyltitaniumtribenzyl, 1,2,3-trimethyl-
4,5,6,7-tetrahydroindenyltitanium trichloride, 1,2,3-
trimethyl-4,5,6,7-tetrahydroindenyltitaniumtrimethyl,
1,2,3-trimethyl-4,5,6,7-tetrahydroindenyltitanium
trimethoxide, 1,2,3-trimethyl-4,5,6,7-
tetrahydroindenyltitaniumtribenzyl, 1-ethyl-4,5,6,7-
tetrahydroindenyltitanium trichloride, 1-ethyl-4,5,6,7-
tetrahydroindenyltitaniumtrimethyl, 1-ethyl-4,5,6,7-
tetrahydroindenyltitanium trimethoxide, 1-ethyl-4,5,6,7-
tetrahydroindenyltitaniumtribenzyl, 1-ethyl-2-methyl-
4,5,6,7-tetrahydroindenyltitanium trichloride, 1-ethyl-2-
methyl-4,5,6,7-tetrahydroindenyltitaniumtrimethyl, 1-
ethyl-2-methyl-4,5,6,7-tetrahydroindenyltitanium

trimethoxide, 1-ethyl-2-methyl-4,5,6,7-tetrahydroindenyltitaniumtribenzyl, 1-ethyl-3-methyl-4,5,6,7-tetrahydroindenyltitanium trichloride, 1-ethyl-3-methyl-4,5,6,7-tetrahydroindenyltitanium trichloride, 1-ethyl-3-methyl-4,5,6,7-tetrahydroindenyltitaniumtrimethyl, 1-ethyl-3-methyl-4,5,6,7-tetrahydroindenyltitanium trimethoxide, 1-ethyl-3-methyl-4,5,6,7-tetrahydroindenyltitaniumtribenzyl, 1-ethyl-2,3-dimethyl-4,5,6,7-tetrahydroindenyltitanium trichloride, 1-ethyl-2,3-dimethyl-4,5,6,7-tetrahydroindenyltitaniumtrimethyl, 1-ethyl-2,3-dimethyl-4,5,6,7-tetrahydroindenyltitanium trimethoxide, 1-ethyl-2,3-dimethyl-4,5,6,7-tetrahydroindenyltitaniumtribenzyl, 1,2-diethyl-4,5,6,7-tetrahydroindenyltitanium trichloride, 1,2-diethyl-4,5,6,7-tetrahydroindenyltitaniumtrimethyl, 1,2-diethyl-4,5,6,7-tetrahydroindenyltitanium trimethoxide, 1,2-diethyl-4,5,6,7-tetrahydroindenyltitaniumtribenzyl, 1,2-diethyl-3-methyl-4,5,6,7-tetrahydroindenyltitanium trichloride, 1,2-diethyl-3-methyl-4,5,6,7-tetrahydroindenyltitaniumtrimethyl, 1,2-diethyl-3-methyl-4,5,6,7-tetrahydroindenyltitanium trimethoxide, 1,2-diethyl-3-methyl-4,5,6,7-tetrahydroindenyltitaniumtribenzyl, 1,3-diethyl-4,5,6,7-tetrahydroindenyltitanium trichloride, 1,3-diethyl-4,5,6,7-tetrahydroindenyltitaniumtrimethyl, 1,3-diethyl-

4,5,6,7-tetrahydroindenyltitanium trimethoxide, 1,3-
diethyl-4,5,6,7-tetrahydroindenyltitaniumtribenzyl, 1,3-
diethyl-2-methyl-4,5,6,7-tetrahydroindenyltitanium
trichloride, 1,3-diethyl-2-methyl-4,5,6,7-
tetrahydroindenyltitaniumtrimethyl, 1,3-diethyl-2-methyl-
4,5,6,7-tetrahydroindenyltitanium trimethoxide, 1,3-
diethyl-2-methyl-4,5,6,7-
tetrahydroindenyltitaniumtribenzyl, 1,2,3-triethyl-
4,5,6,7-tetrahydroindenyltitanium trichloride, 1,2,3-
triethyl-4,5,6,7-tetrahydroindenyltitaniumtrimethyl,
1,2,3-triethyl-4,5,6,7-tetrahydroindenyltitanium
trimethoxide, 1,2,3-triethyl-4,5,6,7-
tetrahydroindenyltitaniumtribenzyl, 2-ethyl-4,5,6,7-
tetrahydroindenyltitanium trichloride, 2-ethyl-4,5,6,7-
tetrahydroindenyltitaniumtrimethyl, 2-ethyl-4,5,6,7-
tetrahydroindenyltitanium trimethoxide, 2-ethyl-4,5,6,7-
tetrahydroindenyltitaniumtribenzyl, 1-methyl-2-ethyl-
4,5,6,7-tetrahydroindenyltitanium trichloride, 1-methyl-2-
ethyl-4,5,6,7-tetrahydroindenyltitaniumtrimethyl, 1-
methyl-2-ethyl-4,5,6,7-tetrahydroindenyltitanium
trimethoxide, 1-methyl-2-ethyl-4,5,6,7-
tetrahydroindenyltitaniumtribenzyl, 1,3-dimethyl-2-ethyl-
4,5,6,7-tetrahydroindenyltitanium trichloride, 1,3-
dimethyl-2-ethyl-4,5,6,7-
tetrahydroindenyltitaniumtrimethyl, 1,3-dimethyl-2-ethyl-

4,5,6,7-tetrahydroindenyltitanium trimethoxide, 1,3-
 dimethyl-2-ethyl-4,5,6,7-
 tetrahydroindenyltitaniumtribenzyl, 1,2,3,4-
 tetrahydrofluorenyltitanium trichloride, 1,2,3,4-
 tetrahydrofluorenyltitaniumtrimethyl, 1,2,3,4-
 tetrahydrofluorenyltitanium trimethoxide, 1,2,3,4-
 tetrahydrofluorenyltitaniumtribenzyl, 9-methyl-1,2,3,4-
 tetrahydrofluorenyltitanium trichloride, 9-methyl-1,2,3,4-
 tetrahydrofluorenyltitaniumtrimethyl, 9-methyl-1,2,3,4-
 tetrahydrofluorenyltitanium trimethoxide, 9-methyl-
 1,2,3,4-tetrahydrofluorenyltitaniumtribenzyl, 9-ethyl-
 1,2,3,4-tetrahydrofluorenyltitanium trichloride, 9-ethyl-
 1,2,3,4-tetrahydrofluorenyltitaniumtrimethyl, 9-ethyl-
 1,2,3,4-tetrahydrofluorenyltitanium trimethoxide, 9-ethyl-
 1,2,3,4-tetrahydrofluorenyltitaniumtribenzyl,
 1,2,3,4,5,6,7,8-octahydrofluorenyltitanium trichloride,
 1,2,3,4,5,6,7,8-octahydrofluorenyltitaniumtrimethyl,
 1,2,3,4,5,6,7,8-octahydrofluorenyltitanium trimethoxide,
 1,2,3,4,5,6,7,8-octahydrofluorenyltitaniumtribenzyl, 9-
 methyl-1,2,3,4,5,6,7,8-octahydrofluorenyltitanium
 trichloride, 9-methyl-1,2,3,4,5,6,7,8-
 octahydrofluorenyltitaniumtrimethyl, 9-methyl-
 1,2,3,4,5,6,7,8-octahydrofluorenyltitanium trimethoxide,
 9-methyl-1,2,3,4,5,6,7,8-octahydrofluorenyltitanium
 trichloride, 9-ethyl-1,2,3,4,5,6,7,8-

(IV) In the transition metal compounds of formula (I-6), M^2 represents a transition metal of Groups 8 to 10 of the Periodic Table, concretely including iron, cobalt, nickel, palladium, platinum, etc. Of those, preferred are nickel and palladium. L^1 and L^2 each represents a coordination-bonding ligand; and X^1 and Y^1 each represent a covalent-bonding or ionic-bonding ligand. As mentioned hereinabove, X^1 and Y^1 include, for example, a hydrogen atom, a halogen atom, a hydrocarbon group having from 1 to 20, preferably from 1 to 10 carbon atoms, an alkoxy group having from 1 to 20, preferably from 1 to 10 carbon atoms, an amino group, a phosphorus-containing hydrocarbon group having from 1 to 20, preferably from 1 to 12 carbon atoms (e.g., a diphenylphosphine group, etc.), a silicon-containing hydrocarbon group having from 1 to 20, preferably from 1 to 12 carbon atoms (e.g., a trimethylsilyl group, etc.), and a boron compound residue having a hydrocarbon group with from 1 to 20, preferably from 1 to 12 carbon atoms or having halogens (e.g., $B(C_6H_5)_4$, BF_4). Of those, preferred are halogen atoms and hydrocarbon groups. X^1 and Y^1 may be the same or different ones. Specific examples of L^1 and L^2 include triphenylphosphine, acetonitrile, benzonitrile, 1,2-bisdiphenylphosphinoethane, 1,3-bisdiphenylphosphinopropane, 1,1'-bisdiphenylphosphinoferrocene, cyclooctadiene, pyridine,

0986931-075601

0986931-075601

0986931-075601



0986931-075601

0986931-075601

or branched alkyl group having from 1 to 20 carbon atoms or a cycloalkyl group having from 3 to 20 carbon atoms, concretely including a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, a pentyl group, a hexyl group, an octyl group, a decyl group, a tetradecyl group, a hexadecyl group, an octadecyl group, a cyclopentyl group, a cyclohexyl group, and a cyclooctyl group, etc. Into the ring of the cycloalkyl group, a suitable substituent such as a lower alkyl group or the like may be introduced. The aromatic group having a hydrocarbon group on the ring and having from 7 to 20 carbon atoms in total includes, for example, phenyl and naphthyl groups with at least one linear, branched or cyclic C1-10 alkyl group being on the aromatic ring. For R^{17} and R^{20} , preferred is an aromatic group having a hydrocarbon group on the ring, and especially preferred is a 2,6-diisopropylphenyl group. R^{17} and R^{20} may be the same or different.

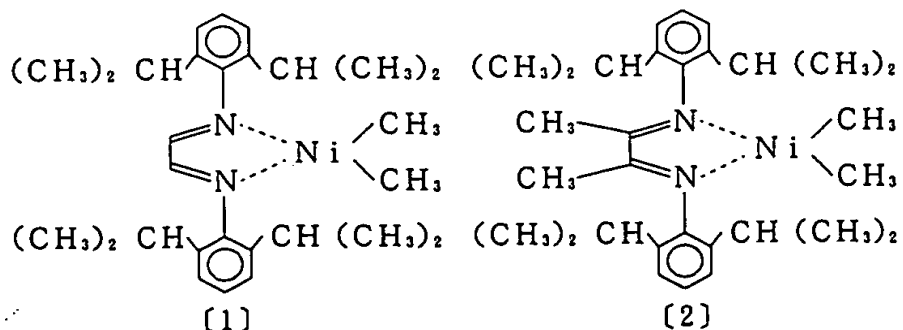
The hydrocarbon group having from 1 to 20 carbon atoms for R^{18} and R^{19} includes, for example, a linear or branched alkyl group having from 1 to 20 carbon atoms, a cycloalkyl group having from 3 to 20 carbon atoms, an aryl group having from 6 to 20 carbon atoms, and an aralkyl group having from 7 to 20 carbon atoms. For examples of the linear or branched alkyl group having from 1 to 20 carbon atoms and the cycloalkyl group having from 3 to 20 carbon atoms for R^{18} and R^{19} , referred to

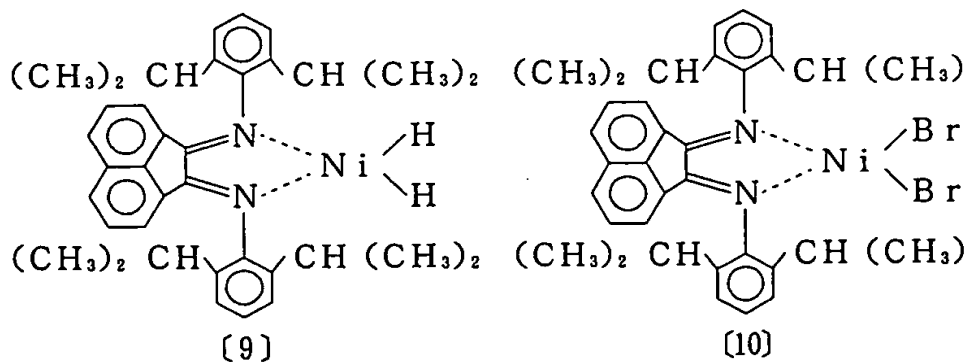
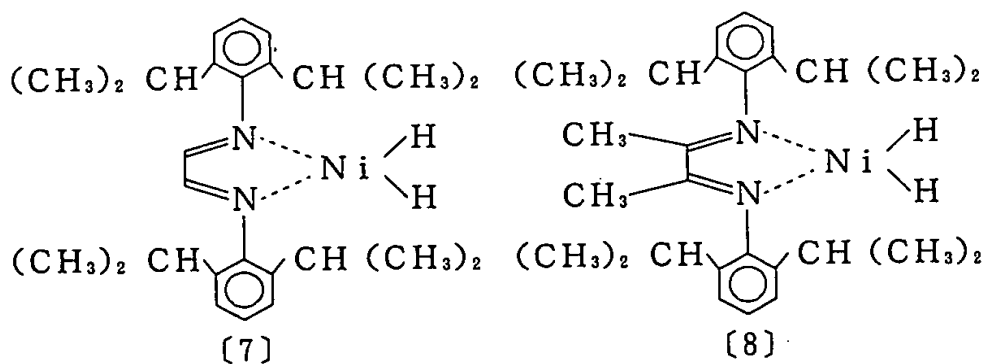
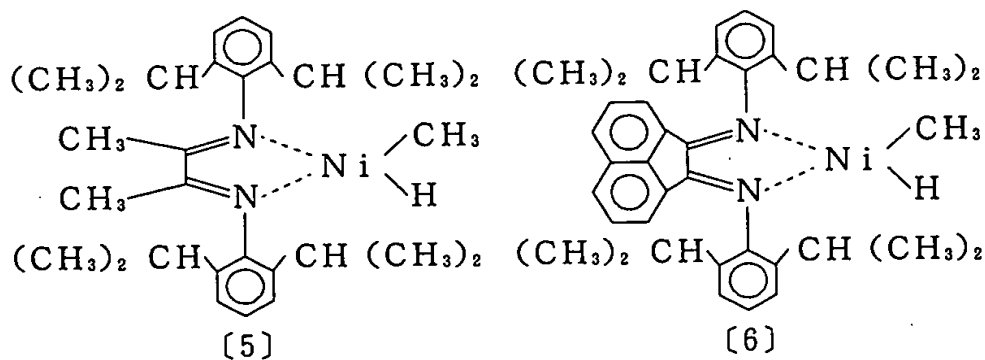
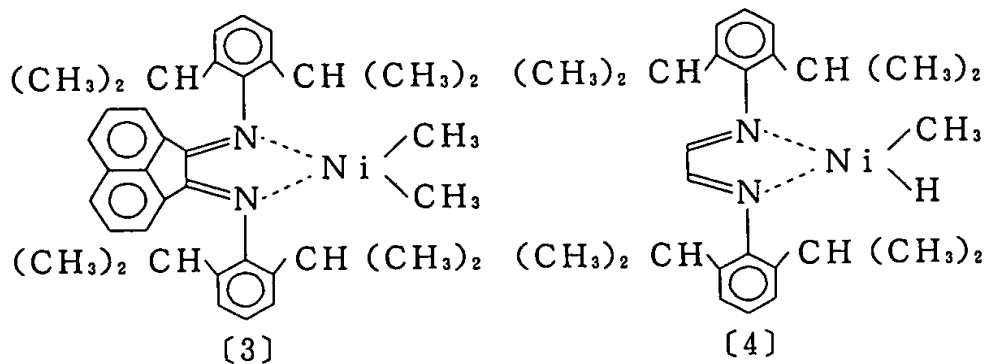
are those of the C1-20 aliphatic hydrocarbon group mentioned hereinabove for R^{17} and R^{20} . The aryl group having from 6 to 20 carbon atoms includes, for example, a phenyl group, a tolyl group, a xylyl group, a naphthyl group, a methylnaphthyl group, etc.; and the aralkyl group having from 7 to 20 carbon atoms includes, for example, a benzyl group, a phenethyl group, etc. R^{17} and R^{18} may be the same or different, and may be bonded to each other to form a ring.

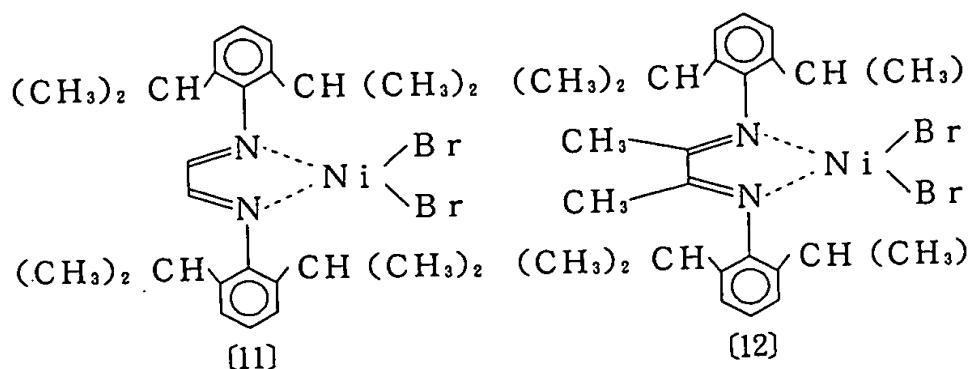
For examples of the hydrocarbon group having from 1 to 20 carbon atoms for X and Y, referred to are those of the C1-20 hydrocarbon group mentioned hereinabove for R^{18} and R^{19} . For X and Y, especially preferred is a methyl group. X and Y may be the same or different.

The transition metal of Groups 8 to 10 of the Periodic Table for M^2 includes, for example, nickel, palladium, platinum, iron, cobalt, rhodium, ruthenium, etc. Preferred are nickel and palladium.

Specific examples of the complex compounds of formula (I-7) are compounds of the following formulae [1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11] and [12].







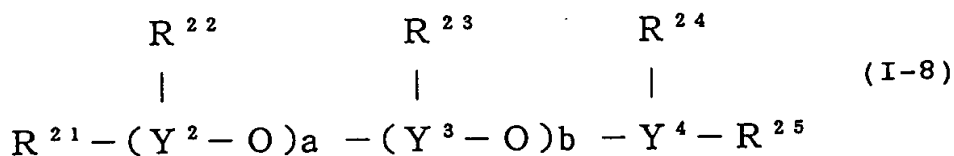
Specific examples of the transition metal compounds of formula (I-7) include dibromobistriphenylphosphine nickel, dichlorobistriphenylphosphine nickel, dibromodiacetonitrile nickel, dibromodibenzonitrile nickel, dibromo(1,2-bisdiphenylphosphinoethane) nickel, dibromo(1,3-bisdiphenylphosphinopropane) nickel, dibromo(1,1'-diphenylbisphosphinoferrocene) nickel, dimethylbisdiphenylphosphine nickel, dimethyl(1,2-bisdiphenylphosphinoethane) nickel, methyl(1,2-bisdiphenylphosphinoethane)nickel tetrafluoroborate, (2-diphenylphosphino-1-phenylethyleneoxy)phenylpyridine nickel, dichlorobistriphenylphosphine palladium, dichlorodibenzonitrile palladium, dichlorodiacetonitrile palladium, dichloro(1,2-bisdiphenylphosphinoethane) palladium, bistrisphenylphosphinopalladium bistetrafluoroborate, bis(2,2'-bipyridino)methyliron tetrafluoroborate etherate, etc.

Of those, preferred are cationic complexes such as methyl(1,2-bisdiphenylphosphinoethano)nickel tetrafluoroborate, bistrisphenylphosphinopalladium bistetrafluoroborate, and bis(2,2'-bipyridino)methyliron tetrafluoroborate etherate.

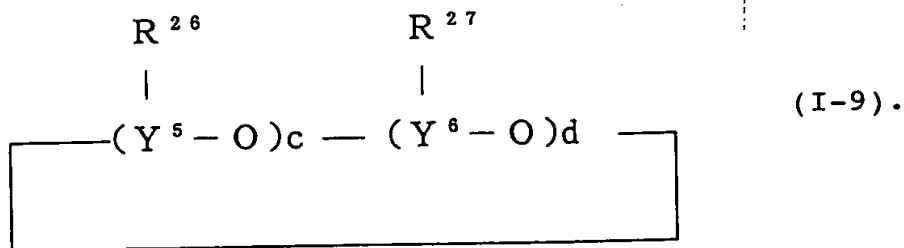
In the invention, one or more of the complex compounds noted above may be used either singly or as combined.

(B) Oxygen-containing compound:

Herein used are oxygen-containing compounds of a general formula (I-8):



and/or those of a general formula (I-9):



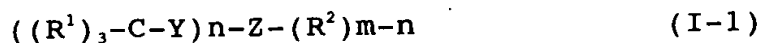
In formulae (I-8) and (I-9), R^{21} to R^{27} each represent an alkyl group having from 1 to 8 carbon atoms, concretely

including a methyl group, an ethyl group, an n-propyl group, an isopropyl group, all types of butyl groups, all types of pentyl groups, all types of hexyl group, all types of heptyl groups, and all types of octyl groups. R^{21} to R^{27} may be the same or different; and R^{26} and R^{27} may be the same or different. Y^2 to Y^6 each represent an element of Group 13 of the Periodic Table, concretely including B, Al, Ga, In and Tl. Of these, preferred are B and Al. Y^2 to Y^4 may be the same or different; and Y^5 and Y^6 may be the same or different. a to d each indicates a number of from 0 to 50, but (a + b) and (c + d) each must be at least 1. a to d each preferably falls between 1 and 20, more preferably between 1 and 10, even more preferably between 1 and 5.

As the oxygen-containing compound for the catalyst component, preferred are alkylaluminoxanes. Preferred examples of the compound are methylaluminoxane and isobutylaluminoxane.

Component (C):

This is a compound of the following general formula (I-1):



wherein R^1 represents an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy

group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, R^1 's may be the same or different, and R^1 's may be optionally bonded to each other to form a cyclic structure; Y represents an element of Group 16; Z represents a metal element of Groups 2 to 13; R^2 represents a hydrocarbon group; m is an integer, indicating the valency of the metal element Z; and n is an integer of from 1 to (m-1),

Especially preferred are the following compounds: (1) Y is oxygen and Z is aluminium; (2) at least one of three R^1 's is an aromatic hydrocarbon group having from 6 to 30 carbon atoms; (3) three R^1 's are all hydrocarbon groups each having at least one carbon atom; (4) three R^1 's are all hydrocarbon groups each having from 4 to 30 carbon atoms; (5) three R^1 's are all aromatic hydrocarbon groups each having from 6 to 30 carbon atoms, preferably phenyl groups; (6) R^2 is an alkyl group having at least 2 carbon atoms.

Concretely, more preferred those where R^1 's are all phenyl groups, Y is oxygen, Z is aluminium, $n = 1$, and R^2 is an isobutyl group.

The compounds for the component (C) are not specifically defined for their production method, so far as they have the structure of the formula mentioned above, but preferred are those produced by reacting <1> a compound of a general formula, $(R^1)_3-C-OR^3$ or <1> at least one selected from compounds of a general formula, $(R^1)_3-C-OR^3$, R^4-CO-R^5 or $R^6-CO-OR^7$, with <2> a

00059331.072601

compound of a general formula, $Z(R^2)_m$. (In these formulae, R^1 represents an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, R^1 's may be the same or different, and R^1 's may be optionally bonded to each other to form a cyclic structure; R^3 , R^4 , R^5 , R^6 and R^7 each represent a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, and R^3 , R^4 , R^5 , R^6 and R^7 may be the same or different; Z represents a metal element of Groups 2 to 13; m is an integer, indicating the valency of the metal element Z ; and R^2 represents a hydrocarbon group.

Concretely, they are reaction products of at least one selected from alcohols, ethers, aldehydes, ketones, carboxylic acids and carboxylates, with an aluminium compound. Preferred are reaction products of alcohols with an aluminium compound. For these, preferred are the following: (1) at least one of three R^1 's for (R^1) , is an aromatic hydrocarbon

09869331-072601

group having from 6 to 30 carbon atoms; (2) three R^1 's for (R^1), are all hydrocarbon groups each having at least one carbon atom; (3) three R^1 's for (R^1), are all hydrocarbon groups each having from 4 to 30 carbon atoms; (4) three R^1 's for (R^1), are all aromatic hydrocarbon groups each having from 6 to 30 carbon atoms, preferably phenyl groups; (5) R^2 is an alkyl group having at least 2 carbon atoms. Concretely, more preferred are those where R^1 's are all phenyl groups, and R^2 is an isobutyl group. Most preferred is a reaction product of triphenylmethyl alcohol with triisobutylaluminium.

The reaction condition for the compound <1> and the compound <2> is not specifically defined, but is preferably as follows: They are blended in a ratio by mol, compound <1>/compound <2> falling between 1/0.1 and 1/10, more preferably between 1/0.5 and 1/2, even more preferably between 1/0.8 and 1/1.2. The reaction temperature falls between -80°C and 300°C, more preferably between -10°C and 50°C. The solvent for the reaction is not also specifically defined, but preferred are toluene, ethylbenzene and the like.

In place of using the compound of the above-mentioned general formula as the component (C), a compound of the following (C1) and a compound of the following (C2) may be directly added to the site of catalyst production or to the site of polymerization to form the component (C) in situ. In this case, the catalyst components are the transition metal

compound (A), the oxygen-containing compound (B), the compounds (C1) and (C2), and optionally an alkylating agent (D).

(C1) is a compound of a general formula, $(R^1)_3-C-OR^3$, or at least one selected from compounds of a general formula, $(R^1)_3-C-OR^3$, R^4-CO-R^5 or $R^6-CO-OR^7$; and (C2) is a compound of a general formula, $Z(R^2)_m$.

In these formulae, R^1 represents an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, R^1 's may be the same or different, and R^1 's may be optionally bonded to each other to form a cyclic structure; R^3 , R^4 , R^5 , R^6 and R^7 each represent a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, and R^3 , R^4 , R^5 , R^6 and R^7 may be the same or different; Z represents a metal element of Groups 2 to 13; m is an integer,

indicating the valency of the metal element Z; and R² represents a hydrocarbon group.

Concretely, (C1) is at least one selected from alcohols, ethers, aldehydes, ketones, carboxylic acids and carboxylates, preferably from alcohols; and (C2) is an aluminium compound. For these, preferred are the following: (1) at least one of three R¹'s for (R¹)₃, is an aromatic hydrocarbon group having from 6 to 30 carbon atoms; (2) three R¹'s for (R¹)₃, are all hydrocarbon groups each having at least one carbon atom; (3) three R¹'s for (R¹)₃, are all hydrocarbon groups each having from 4 to 30 carbon atoms; (4) three R¹'s for (R¹)₃, are all aromatic hydrocarbon groups each having from 6 to 30 carbon atoms, preferably phenyl groups; (5) R² is an alkyl group having at least 2 carbon atoms. More concretely, the most preferred combination is (C1) of triphenylmethyl alcohol and (C2) of triisobutylaluminium.

(D) Alkylating agent:

The catalyst of the invention for production of olefinic polymers optionally contains an alkylating agent. Various types of alkylating agents are known and are usable in the invention, including, for example, alkyl group-having aluminium compounds of a general formula (I-12):



wherein R²⁸ and R²⁹ each represent an alkyl group having from 1 to 8, preferably from 1 to 4 carbon atoms; X represents

a hydrogen atom or a halogen atom; $0 < m \leq 3$, but preferably m is 2 or 3, most preferably 3; $0 \leq n < 3$, but preferably n is 0 or 1;

alkyl group-having magnesium compounds of a general formula (I-13):

wherein R²⁸ has the same meaning as above; and
alkyl group-having zinc compounds of a general formula (I-
14):

wherein R^{28} has the same meaning as above.

hydride, diethylaluminium hydride, diisobutylaluminium hydride, etc. Further mentioned are dialkylmagnesiums such as dimethylmagnesium, diethylmagnesium, di-n-propylmagnesium, diisopropylmagnesium, etc.; dialkylzincs such as dimethylzinc, diethylzinc, di-n-propylethylzinc, diisopropylzinc, etc.

2. Method for producing catalyst:

(1) Order of contacting constituent components:

To produce the catalyst of the invention, the order of contacting the constituent components with each other is not specifically defined. For example, the components may be contacted with each other in the following manner.

(i) For producing the catalyst comprising the component (A), the component (B) and the component (C), for example, employable is <1> a method of first contacting the component (A) with the component (B), followed by further contacting it with the component (C); <2> a method of first contacting the component (A) with the component (C) followed by further contacting it with the component (B); <3> a method of first contacting the component (B) with the component (C) followed by further contacting it with the component (A); or <4> a method of contacting the three components all together.

When the catalyst contains the optional component (D), the order of contacting the component (D) with the other components is not specifically defined. For example, in the process of producing the catalyst, the component (A) may be

contacted with the component (D); or the component (B) may be contacted with the component (D); or the component (C) may be contacted with the component (D). As the case may be, the components (A), (B) and (D) are first contacted all together with each other and then with the component (C). (ii) For producing the catalyst comprising the component (A), the component (B), the component (C1) and the component (C2), the order of contacting these components with each other is not also specifically defined, like in the case (i). Preferably, however, the component (C1) and the component (C2) are first contacted with each other prior to being contacted with the other components. The same as in the case (i) shall apply also to the case (ii) of producing the catalyst containing the optional component (D).

(2) Blend ratio of constituent components:

<1> Regarding the ratio by mol of the component (A) to the component (B), referred to is a case where an organoaluminium compound is used as the oxygen-containing compound of the component (B). In that case, the molar ratio of the component (A) to the component (B) may fall between 1/1 and 1/10,000, but preferably between 1/10 and 1/1,000, in terms of the molar ratio to the aluminium atom in (B).

<2> Regarding the ratio by mol of the component (A) to the component (C), referred to is a case where an aluminium compound is used as the component (C). In that case, the molar

ratio of the component (A) to the component (C) may fall between 1/0.5 and 1/1,000, but preferably between 1/0.8 and 1/100, more preferably between 1/1 and 1/100, in terms of the molar ratio to the aluminium atom in (C). Regarding the ratio by mol of the component (A) to the component (D), referred to is a case where an aluminium compound is used as the component (D). In that case, the molar ratio of the component (A) to the component (D) may fall between 1/0.5 and 1/1,000, but preferably between 1/1 and 1/100, in terms of the molar ratio to the aluminium atom in (D).

<3> Where the catalyst contains a combination of the component (C1) and the component (C2), but not the component (C), the molar ratio of (C1) to (C2) may fall between 1/0.1 and 1/50, precisely between 1/0.1 and 1/10, or between 1/0.5 and 1/20, or between 1/0.8 and 1/10, or between 1/0.5 and 1/2, or between 1/0.8 and 1/1.2, but most preferably between 1/0.8 and 1/10.

Regarding the ratio by mol of the component (A) to the component (C2), referred to is a case where an aluminium compound is used as the component (C2). In that case, the molar ratio of the component (A) to the component (C2) may fall between 1/0.5 and 1/1,000, but preferably between 1/1 and 1/100, in terms of the molar ratio to the aluminium atom in (C2). Regarding the blend ratio of the component (D), the same as in the case <2> shall apply also to the case <3>.

(3) Condition for contacting constituent components:

To produce the catalyst, the constituent components may be contacted with each other in an inert atmosphere of nitrogen or the like, at a temperature not higher than the temperature at which the catalyst is used for polymerization. As the case may be, they may be contacted with each other at a temperature falling between -30 and 200°C .

(4) In the invention, the components constituting the catalyst, especially the component (B) may be carried on a suitable carrier. Any types of carriers are usable with no specific limitation, but preferred are inorganic carriers such as inorganic oxides, etc. Concretely, the inorganic oxides include SiO_2 , Al_2O_3 , TiO_2 , Fe_2O_3 , B_2O_3 , CaO , ZnO , BaO , ThO_2 , silica-alumina, zeolite, ferrite, glass fibers, etc. Of those, especially preferred are SiO_2 and Al_2O_3 . The inorganic oxide carriers may contain a small amount of carbonates, nitrates, sulfates, etc. For their properties, the carriers are not specifically defined. Generally, the carriers have a mean particle size of from 1 to $300\text{ }\mu\text{m}$, but preferably from 10 to $200\text{ }\mu\text{m}$, more preferably from 20 to $100\text{ }\mu\text{m}$.

II. Method for producing olefinic polymers:

1. Monomers to be polymerized:

In the method of the invention for producing olefinic polymers, used is the above-mentioned catalyst for polymerization of olefins. The catalyst is favorable to

homopolymerization of olefins and to copolymerization of olefins with other olefins (that is, copolymerization of different types of olefins).

Olefins for the method are not specifically defined, but preferred are α -olefins having from 2 to 20 carbon atoms. Especially preferred are ethylene and propylene.

They include α -olefins such as ethylene, propylene, 1-butene, 3-methyl-1-butene, 4-methyl-1-butene, 4-phenyl-1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 3,3-dimethyl-1-pentene, 3,4-dimethyl-1-pentene, 4,4-dimethyl-1-pentene, 1-hexene, 4-methyl-1-hexene, 5-methyl-1-hexene, 6-phenyl-1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, vinylcyclohexane, etc.; halogen-substituted α -olefins such as hexafluoropropene, tetrafluoroethylene, 2-fluoropropene, fluoroethylene, 1,1-difluoroethylene, 3-fluoropropene, trifluoroethylene, 3,4-dichloro-1-butene, etc.; and cyclic olefins such as cyclopentene, cyclohexene, norbornene, 5-methylnorbornene, 5-ethylnorbornene, 5-propylnorbornene, 5,6-dimethylnorbornene, 5-benzylnorbornene, etc.

In the invention, one or more olefins such as those mentioned above may be (co)polymerized in any desired combination.

2. Polymerization condition:

In the invention, the polymerization catalyst may be

component (C) or with the components (C1) and (C2) in a different reactor, and the two blends in different reactors are mixed just before the start of polymerization of the monomers. Having been thus blended, the monomers begin to polymerize in the presence of the catalyst formed in situ.

For the polymerization, a solvent may be used. The solvent includes hydrocarbons and halogenohydrocarbons such as benzene, toluene, xylene, n-hexane, n-heptane, cyclohexane, methylene chloride, chloroform, 1,2-dichloroethane, chlorobenzene, etc. One or more of these compounds may be used either singly or as combined for the solvent. Depending on their type, the monomers to be polymerized could serve as a polymerization solvent.

The amount of the catalyst to be used for the polymerization is preferably so controlled that the component (A) may fall generally between 0.1 and 100 μ moles, but preferably between 0.5 and 25 μ moles, in one liter of the solvent, in view of the polymerization activity and the reactor efficiency.

Regarding the polymerization condition, the pressure may fall generally between normal pressure and 2000 kg/cm²G (196 MPaG). The reaction temperature may fall generally between -50 and 250°C. For controlling the molecular weight of the polymer to be produced, the type and the amount of the catalyst components to be used and the polymerization temperature shall be suitably controlled, or hydrogen may be

introduced into the polymerization system.

The invention is described in more detail with reference to the following Examples, which, however, are not intended to restrict the scope of the invention.

The stereospecificity [mmmm] of the polymer produced was determined as follows: A sample of the polymer was dissolved in a mixed solvent of 1,2,4-trichlorobenzene and heavy benzene (90/10, by volume), and subjected to a proton complete decoupling method for ^{13}C -NMR (using JEOL' LA-500) at 130°C. Based on the signals for the methyl group obtained in the method, the stereospecificity [mmmm] of the sample was determined. The stereospecificity was proposed by A. Zambelli et al. in *Macromolecules*, 6, 925 (1973), and it indicates the isotactic fraction [mmmm] in the pentad units of a polypropylene molecular chain as measured in ^{13}C nuclear magnetic resonance spectrometry. For the attribution of the peaks seen in the ^{13}C nuclear magnetic resonance spectrometry, referred to was the A. Zambelli et al's proposal in *Macromolecules*, 8, 687 (1975).

The molecular weight (M_w) of the polymer produced and the molecular weight distribution (M_w/M_n) thereof were measured through GPC.

[Example I-1]

(1) Preparation of component (C):

0.875 ml of 2 M triisobutylaluminium was added to a

toluene solution of 455 mg (1.75 mmols) of triphenylmethanol at -78°C , and stirred at room temperature for 24 hours. The concentration of the component (C) thus formed was 0.1 mols/liter.

Through $^1\text{H-NMR}$, the product was confirmed to have the component (C) formed therein.

(2) Preparation of silica-carried methylaluminoxane:

27.1 g of SiO_2 (Fuji Silicia's P-10) was put into a 500 ml Schlenk, and dried at 200°C under pressure for 4 hours. The baked SiO_2 weighed 25.9 g. The baked SiO_2 was put into 400 ml of toluene cooled at -78°C in a dry ice/methanol bath, and stirred. With stirring, 145.5 ml of a solution of methylaluminoxane/toluene (1.5 mols/liter) was dropwise added to the resulting suspension, which took 1 hour to the end. After left as such for 4 hours, this was heated from -78°C up to 20°C over a period of 6 hours, and then further left as it was for 4 hour. Next, this was heated from 20°C up to 80°C over a period of 1 hour, and then left at 80°C for 4 hours. Through the process, the reaction between silica and methylaluminoxane was completed. The resulting suspension was filtered at 60°C , and the solid residue was washed twice with 400 ml of toluene at 60°C . The thus-washed solid was dried at 60°C under reduced pressure for 4 hours, whereby was obtained 33.69 g of silica-carried methylaluminoxane in which the proportion of methylaluminoxane was 23.12 % by weight. N-heptane was added

to all the silica-carried methylaluminoxane to be 500 ml in total. The suspension thus prepared had a methylaluminoxane concentration of 0.27 mols/liter.

(3) Polymerization of propylene:

400 ml of heptane was put into a one-liter stainless autoclave, to which were added 0.5 mmols of triisobutylaluminium, 50 μ mol of the solution of the component (C) prepared in the step (1), 0.25 mmols, in terms of aluminium atom, of the silica-carried methylaluminoxane prepared in the step (2), and 1 μ mol of dimethylsilylenebis(2-methyl-4,5-benzoindenyl)zirconium dichloride after having been pre-contacted with each other in toluene for 5 minutes to form a catalyst. Propylene gas was introduced into the autoclave to have a total pressure of 0.785 MPaG (8.0 kg/cm²G). During its polymerization, propylene was continuously introduced into the autoclave via a pressure controlling unit so as to have all the time a constant pressure. In that condition, propylene was polymerized at 70°C for 60 minutes. The resulting product was dried under reduced pressure. Thus obtained, the propylene polymer weighed 33.2 g. Its limiting viscosity (at 135°C in tetralin), $[\eta]$, was 1.2; its weight-average molecular weight (M_w) was 1,070,000; its molecular weight distribution (M_w/M_n) was 2.07; and its stereospecificity was 97.2 %.

[Comparative Example I-1]

(1) Blending of component of catalyst for polymer production:

This is the same as in Example I-1 (2).

(2) Polymerization of olefin:

This is the same as in Example I-1, except for the step of Example I-1 (3). In this, the component (C) prepared in Example I-1 (1) was not added to the polymerization system.

Thus obtained, the propylene polymer weighed 16.0 g. Its limiting viscosity (at 135°C in tetralin), $[\eta]$, was 1.3; its weight-average molecular weight (M_w) was 1,100,000; its molecular weight distribution (M_w/M_n) was 2.04; and its stereospecificity was 96.8 %.

[Example I-2]

(1) Preparation of component (C):

0.875 ml of 2 M triisobutylaluminium was added to a toluene solution of 1.75 mmols of tricyclohexylmethanol (from Across) at -78°C, and stirred at room temperature for 24 hours. The concentration of the component (C) thus formed was 0.1 mols/liter.

Through $^1\text{H-NMR}$, the product was confirmed to have the component (C) formed therein.

(2) Polymerization of propylene:

400 ml of heptane was put into a one-liter stainless autoclave, to which were added 0.5 mmols of triisobutylaluminium, 50 μmols of the solution of the component (C) prepared in the step (1), 0.25 mmols, in terms of aluminium atom, of the silica-carried methylaluminoxane prepared in the

step of Example I-1 (2), and 1 μmol of dimethylsilylenebis(2-methyl-4,5-benzoindenyl)zirconium dichloride after having been pre-contacted with each other in toluene for 5 minutes to form a catalyst. Propylene gas was introduced into the autoclave to have a total pressure of 0.785 MPaG (8.0 kg/cm²G). During its polymerization, propylene was continuously introduced into the autoclave via a pressure controlling unit so as to have all the time a constant pressure. In that condition, propylene was polymerized at 70°C for 60 minutes. The resulting product was dried under reduced pressure. Thus obtained, the propylene polymer weighed 28.4 g. Its weight-average molecular weight (Mw) was 1,190,000; its molecular weight distribution (Mw/Mn) was 2.04; and its stereospecificity was 97.1 %.

[Example I-3]

(1) Polymerization of ethylene-1-octene:

360 ml of toluene, 40 ml of 1-octene, 0.5 ml of a toluene solution of 1 M triisobutylaluminium, 50 μmol s of the solution of the component (C) prepared in the step of Example I-1 (1), and 0.25 mmols, in terms of aluminium atom, of the silica-carried methylaluminoxane prepared in the step of Example I-1 (2) were put into a 1.6-liter stainless autoclave equipped with a catalyst feeder tube, in that order, and heated up to 70°C. Next, ethylene was introduced into the autoclave to have a pressure of 0.785 MPaG (8.0 kg/cm²G). Next, 1.0 μmol of

09869331-072601

(t-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane-titanium dichloride dissolved in 20 ml of toluene was put into the autoclave via the catalyst feeder tube.

Ethylene was continuously introduced into the autoclave so as to have all the time the constant pressure of 0.785 MPaG (8.0 kg/cm²G), and polymerized for 60 minutes. Next, methanol was added to this to stop the polymerization. A large amount of methanol was added to this, and the polymer formed was separated through filtration, and then dried at 60°C under reduced pressure for 4 hours. Thus obtained, the ethylene-1-octene copolymer weighed 33.8 g. Its weight-average molecular weight (M_w) was 61,000 in terms of ethylene; and its molecular weight distribution (M_w/M_n) was 2.24.

The 1-octene content of the copolymer was 18.4 mol%.

[Comparative Example I-2]

The same process as in Example I-3 was repeated, except that the component (C) was not added to the polymerization system. As a result, herein obtained was 18.3 g of ethylene-1-octene copolymer. Its weight-average molecular weight (M_w) was 64,000 in terms of ethylene; and its molecular weight distribution (M_w/M_n) was 2.06.

The 1-octene content of the copolymer was 18.3 mol%.

[Example I-4]

The same process as in Example I-3 was repeated, except

that 2,2-t-butyl-4,4-methylthiobisphenoxytitanium dichloride was used in place of (t-butylamido)dimethyl(tetramethyl- η 5-cyclopentadienyl)silane-titanium dichloride. As a result, herein obtained was 29.3 g of ethylene-1-octene copolymer. Its weight-average molecular weight (Mw) was 31,000 in terms of ethylene; and its molecular weight distribution (Mw/Mn) was 2.24.

The 1-octene content of the copolymer was 18.4 mol%.
[Comparative Example I-3]

The same process as in Example I-4 was repeated, except that the component (C) was not added to the polymerization system. As a result, herein obtained was 19.4 g of ethylene-1-octene copolymer. Its weight-average molecular weight (Mw) was 34,000 in terms of ethylene; and its molecular weight distribution (Mw/Mn) was 2.06.

The 1-octene content of the copolymer was 18.3 mol%.

[Second aspect of the invention]

In this section, the second aspect of the invention will be simply referred to as "the invention".

I. Catalyst for polymerization of olefins:

1. Components of catalyst for polymerization of olefins:

The catalyst of the invention for polymerization of olefins comprises (A) a transition metal compound, (B) a

compound capable of reacting with a transition metal compound to form an ionic complex, and (C) a compound of formula (II-1) which will be described in detail hereinunder, and optionally (D) an alkylating agent. The constituent components are described below.

(1) (A) Transition metal compound:

For its details, the same as in the section of the first aspect shall directly apply also to this section.

(B) Compound capable of reacting with a transition metal compound to form an ionic complex:

The compound capable of reacting with a transition metal compound to form an ionic complex includes coordination complex compounds that comprise an anion with plural groups bonded to a metal, and a cation, and Lewis acids. Known are various coordination complex compounds that comprise an anion with plural groups bonded to a metal, and a cation. For example, compounds of the following general formula (II-2) or (II-3) are preferably used in the invention.



wherein L^{24} indicates M^{25} , $R^{51}R^{52}M^{26}$ or R^{53}_3C , which will be mentioned hereinafter; L^{23} represents a Lewis base; M^{23} and M^{24} each represent a metal selected from Group 5 to Group 15 of the Periodic Table; M^{25} represents a metal selected from Group 1, and Group 8 to Group 12 of the Periodic Table; M^{26}

group, a p-tolyl group, a benzyl group, a pentafluorophenyl group, a 3,5-di(trifluoromethyl)phenyl group, a 4-tert-butylphenyl group, a 2,6-dimethylphenyl group, a 3,5-dimethylphenyl group, a 2,4-dimethylphenyl group, a 1,2-dimethylphenyl group, etc., as an aryl group having from 6 to 20 carbon atoms, an alkylaryl group or an arylalkyl group; F, Cl, Br, I, as a halogen; and a pentamethylantimonyl group, a trimethylsilyl group, a trimethylgermyl group, a diphenylarsenyl group, a dicyclohexylantimonyl group, a diphenylboryl group, etc., as an organometalloid group. Specific examples of the substituted cyclopentadienyl group for R⁵¹ and R⁵² include a methylcyclopentadienyl group, a butylcyclopentadienyl group, a pentamethylcyclopentadienyl group, etc.

In the invention, concretely, the anion with plural groups bonded to a metal includes B(C₆F₅)₄⁻, B(C₆HF₄)₄⁻, B(C₆H₂F₃)₄⁻, B(C₆H₃F₂)₄⁻, B(C₆H₄F)₄⁻, B[C₆(CF₃)F₄]₄⁻, B(C₆H₅)₄⁻, PF₆⁻, P(C₆F₅)₆⁻, Al(C₆HF₄)₄⁻, etc. The cation includes, for example, Cp₂Fe⁺, (MeCp)₂Fe⁺, (tBuCp)₂Fe⁺, (Me₂Cp)₂Fe⁺, (Me₃Cp)₂Fe⁺, (Me₄Cp)₂Fe⁺, (Me₅Cp)₂Fe⁺, Ag⁺, Na⁺, Li⁺, etc. The other cations include, for example, those from nitrogen-containing compounds, such as pyridinium, 2,4-dinitro-N,N-diethylanilinium, diphenylammonium, p-nitroanilinium, 2,5-dichloroanilinium, p-nitro-N,N-dimethylanilinium, quinolinium, N,N-dimethylanilinium,

00869331.072601

N,N-diethylanilinium, etc.; those from carbenium compounds such as triphenylcarbenium, tri(4-methylphenyl)carbenium, tri(4-methoxyphenyl)carbenium, etc.; alkylphosphonium ions such as CH_3PH_3^+ , $\text{C}_2\text{H}_5\text{PH}_3^+$, $\text{C}_3\text{H}_7\text{PH}_3^+$, $(\text{CH}_3)_2\text{PH}_2^+$, $(\text{C}_2\text{H}_5)_2\text{PH}_2^+$, $(\text{C}_3\text{H}_7)_2\text{PH}_2^+$, $(\text{CH}_3)_3\text{PH}^+$, $(\text{C}_2\text{H}_5)_3\text{PH}^+$, $(\text{C}_3\text{H}_7)_3\text{PH}^+$, $(\text{CF}_3)_3\text{PH}^+$, $(\text{CH}_3)_4\text{P}^+$, $(\text{C}_2\text{H}_5)_4\text{P}^+$, $(\text{C}_3\text{H}_7)_4\text{P}^+$, etc.; arylphosphonium ions such as $\text{C}_6\text{H}_5\text{PH}_3^+$, $(\text{C}_6\text{H}_5)_2\text{PH}_2^+$, $(\text{C}_6\text{H}_5)_3\text{PH}^+$, $(\text{C}_6\text{H}_5)_4\text{P}^+$, $(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\text{PH}^+$, $(\text{CH}_3)(\text{C}_6\text{H}_5)\text{PH}_2^+$, $(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{PH}^+$, $(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)_2\text{P}^+$, etc.

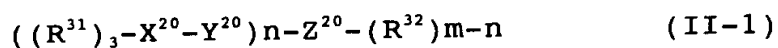
Of the compounds of formulae (II-2) and (II-3), concretely, the following are especially preferred. Preferred examples of the compounds of formula (II-2) include triethylammonium tetraphenylborate, tri(n-butyl)ammonium tetraphenylborate, trimethylammonium tetraphenylborate, triethylammonium tetrakis(pentafluorophenyl)borate, tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate, triethylammonium hexafluoroarsenate, pyridinium tetrakis(pentafluorophenyl)borate, pyrrolinium tetra(pentafluorophenyl)borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, methyldiphenylammonium tetrakis(pentafluorophenyl)borate, etc. Preferred examples of the compounds of formula (II-3) include ferrocenium tetraphenylborate, dimethylferrocenium tetrakis(pentafluorophenyl)borate, ferrocenium tetrakis(pentafluorophenyl)borate, decamethylferrocenium

tetrakis(pentafluorophenyl)borate, acetylferrocenium
 tetrakis(pentafluorophenyl)borate, formylferrocenium
 tetrakis(pentafluorophenyl)borate, cyanoferrocenium
 tetrakis(pentafluorophenyl)borate, silver tetraphenylborate,
 silver tetrakis(pentafluorophenyl)borate, trityl
 tetraphenylborate, trityl tetrakis(pentafluorophenyl)borate,
 silver hexafluoroarsenate, silver hexafluoroantimonate,
 silver tetrafluoroborate, etc.

The Lewis acid includes, for example, $B(C_6F_5)_3$,
 $B(C_6HF_4)_3$, $B(H_2F_3)_3$, $B(C_6H_3F_2)_3$, $B(C_6H_4F)_3$, $B(C_6H_5)_3$, BF_3 ,
 $B[C_6(CF_3)F_4]_3$, PF_5 , $P(C_6F_5)_5$, $Al(C_6HF_4)_3$, etc.

(C) Component:

This is a compound of the following general formula
 (II-1):



wherein R^{31} represents a hydrogen atom, a halogen atom, an
 aliphatic hydrocarbon group having from 1 to 30 carbon atoms,
 an aromatic hydrocarbon group having from 6 to 30 carbon atoms,
 an alkoxy group having from 1 to 30 carbon atoms, an aryloxy
 group having from 6 to 30 carbon atoms, a thioalkoxy group
 having from 1 to 30 carbon atoms, a thioaryloxy group having
 from 6 to 30 carbon atoms, an amino group, an amido group, or
 a carboxyl group, R^{31} 's may be the same or different, and R^{31} 's
 may be optionally bonded to each other to form a cyclic
 structure; X^{20} represents an element of Group 14; Y^{20} represents

an element of Group 16; Z^{20} represents a metal element of Groups 2 to 13; R^{32} represents a hydrocarbon group; m is an integer, indicating the valency of the metal element; and n is an integer of from 1 to $(m-1)$.

Especially preferred are the following compounds: (1) X^{20} is carbon, Y^{20} is oxygen, and Z^{20} is aluminium; (2) at least one of three R^{31} 's is an aromatic hydrocarbon group having from 6 to 30 carbon atoms; (3) three R^{31} 's are all hydrocarbon groups each having at least one carbon atom; (4) three R^{31} 's are all hydrocarbon groups each having from 4 to 30 carbon atoms; (5) three R^{31} 's are all aromatic hydrocarbon groups each having from 6 to 30 carbon atoms, preferably phenyl groups; (6) R^{32} is an alkyl group having at least 2 carbon atoms.

Concretely, more preferred those where R^{31} 's are all phenyl groups, X^{20} is carbon, Y^{20} is oxygen, Z^{20} is aluminium, $n = 1$, and R^{32} is an isobutyl group.

The compounds for the component (C) are not specifically defined for their production method, so far as they have the structure of the formula mentioned above, but preferred are those produced by reacting <1> a compound of a general formula, $(R^{31})_3-C-OR^{33}$ or <1> at least one selected from compounds of a general formula, $(R^{31})_3-C-OR^{33}$, $R^{34}-CO-R^{35}$ or $R^{36}-CO-OR^{37}$, with <2> a compound of a general formula, $Z(R^{32})_m$. (In these formulae, R^{31} represents a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic

hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, R^{31} 's may be the same or different, and R^{31} 's may be optionally bonded to each other to form a cyclic structure; R^{33} , R^{34} , R^{35} , R^{36} and R^{37} each represent a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, and R^{33} , R^{34} , R^{35} , R^{36} and R^{37} may be the same or different; Z^{20} represents a metal element of Groups 2 to 13; m is an integer, indicating the valency of the metal element Z^{20} ; and R^{32} represents a hydrocarbon group.

Concretely, they are reaction products of at least one selected from alcohols, ethers, aldehydes, ketones, carboxylic acids and carboxylates, with an aluminium compound. Preferred are reaction products of alcohols with an aluminium compound. For these, preferred are the following: (1) at least one of three R^{31} 's is an aromatic hydrocarbon group having from 6 to 30 carbon atoms; (2) three R^{31} 's are all hydrocarbon

05869331-072604
T09270-1EE6860

groups each having at least one carbon atom; (3) three R^{31} 's are all hydrocarbon groups each having from 4 to 30 carbon atoms; (4) three R^{31} 's are all aromatic hydrocarbon groups each having from 6 to 30 carbon atoms, preferably phenyl groups; (5) R^{32} is an alkyl group having at least 2 carbon atoms. Concretely, more preferred are those where R^{31} 's are all phenyl groups, and R^{32} is an isobutyl group. Most preferred is a reaction product of triphenylmethyl alcohol with triisobutylaluminium.

The reaction condition for the compound <1> and the compound <2> is not specifically defined, but is preferably as follows: They are blended in a ratio by mol, compound <1>/compound <2> falling between 1/0.1 and 1/10, more preferably between 1/0.5 and 1/2, even more preferably between 1/0.8 and 1/1.2. The reaction temperature falls between -80°C and 300°C, more preferably between -10°C and 50°C; and the reaction time falls between 0.1 minutes and 50 hours, preferably between 0.1 minutes and 3 hours. The solvent for the reaction is not also specifically defined, but is preferably the same one as that for polymerization to be effected in the presence of the catalyst.

In place of using the compound of the above-mentioned general formula as the component (C), a compound of the following (C1) and a compound of the following (C2) may be directly added to the site of catalyst production or to the

09869331-072601

site of polymerization to form the component (C) in situ. In this case, the catalyst components are the transition metal compound (A), the compound (B) capable of reacting with a transition metal to form an ionic complex, the compounds (C1) and (C2), and optionally an alkylating agent (D).

(C1) is a compound of a general formula, $(R^{31})_3-C-OR^{33}$, or at least one selected from compounds of a general formula, $(R^{31})_3-C-OR^{33}$, $R^{34}-CO-R^{35}$ or $R^{36}-CO-OR^{37}$; and (C2) is a compound of a general formula, $Z(R^{32})_m$.

In these formulae, R^{31} represents a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino group, an amido group, or a carboxyl group, R^{31} 's may be the same or different, and R^{31} 's may be optionally bonded to each other to form a cyclic structure; R^{33} , R^{34} , R^{35} , R^{36} and R^{37} each represent a hydrogen atom, a halogen atom, an aliphatic hydrocarbon group having from 1 to 30 carbon atoms, an aromatic hydrocarbon group having from 6 to 30 carbon atoms, an alkoxy group having from 1 to 30 carbon atoms, an aryloxy group having from 6 to 30 carbon atoms, a thioalkoxy group having from 1 to 30 carbon atoms, a thioaryloxy group having from 6 to 30 carbon atoms, an amino

group, an amido group, or a carboxyl group, and R^{33} , R^{34} , R^{35} , R^{36} and R^{37} may be the same or different; Z^{20} represents a metal element of Groups 2 to 13; m is an integer, indicating the valency of the metal element Z^{20} ; and R^{32} represents a hydrocarbon group.

Concretely, (C1) is at least one selected from alcohols, ethers, aldehydes, ketones, carboxylic acids and carboxylates, preferably from alcohols; and (C2) is an aluminium compound. For these, preferred are the following: (1) at least one of three R^{31} 's is an aromatic hydrocarbon group having from 6 to 30 carbon atoms; (2) three R^{31} 's are all hydrocarbon groups each having at least one carbon atom; (3) three R^{31} 's are all hydrocarbon groups each having from 4 to 30 carbon atoms; (4) three R^{31} 's for are all aromatic hydrocarbon groups each having from 6 to 30 carbon atoms, preferably phenyl groups; (5) R^{32} is an alkyl group having at least 2 carbon atoms. More concretely, the most preferred combination is (C1) of triphenylmethyl alcohol and (C2) of triisobutylaluminium.

(D) Alkylating agent:

The catalyst of the invention for production of olefinic polymers optionally contains an alkylating agent. For the details of the alkylating agent, the same as in the section of the first aspect shall directly apply also to this section.

2. Method for producing catalyst:

(1) Order of contacting constituent components:

To produce the catalyst of the invention, the order of contacting the constituent components with each other is not specifically defined. For its details, the same as in the section of the first aspect shall directly apply also to this section.

(2) Blend ratio of constituent components:

<1> Regarding the ratio by mol of the component (A) to the component (B), referred to is a case where an organoaluminium compound is used as the component (B), a compound capable of reacting with a transition metal compound to form an ionic complex. In that case, the molar ratio of the component (A) to the component (B) may fall between 1/1 and 1/10,000, but preferably between 1/10 and 1/1,000, in terms of the molar ratio to the aluminium atom in (B).

<2> Regarding the ratio by mol of the component (A) to the component (C), referred to is a case where an aluminium compound is used as the component (C). In that case, the molar ratio of the component (A) to the component (C) may fall between 1/0.5 and 1/1,000, but preferably between 1/0.8 and 1/100, more preferably between 1/1 and 1/100, in terms of the molar ratio to the aluminium atom in (C). Regarding the ratio by mol of the component (A) to the component (D), referred to is a case where an aluminium compound is used as the component (D). In that case, the molar ratio of the component (A) to the component (D) may fall between 1/0.5 and 1/1,000, but preferably between

1/1 and 1/100, in terms of the molar ratio to the aluminium atom in (D).

<3> Where the catalyst contains a combination of the component (C1) and the component (C2), but not the component (C), the molar ratio of (C1) to (C2) may fall between 1/0.1 and 1/50, precisely between 1/0.1 and 1/10, or between 1/0.5 and 1/20, or between 1/0.8 and 1/10, or between 1/0.5 and 1/2, or between 1/0.8 and 1/1.2, but most preferably between 1/0.8 and 1/10. Regarding the ratio by mol of the component (A) to the component (C2), referred to is a case where an aluminium compound is used as the component (C2). In that case, the molar ratio of the component (A) to the component (C2) may fall between 1/0.5 and 1/1,000, but preferably between 1/1 and 1/100, in terms of the molar ratio to the aluminium atom in (C2). Regarding the blend ratio of the component (D), the same as in the case <2> shall apply also to the case <3>.

(3) Condition for contacting constituent components:

To produce the catalyst, the constituent components may be contacted with each other in an inert atmosphere of nitrogen or the like, at a temperature not higher than the temperature at which the catalyst is used for polymerization. As the case may be, they may be contacted with each other at a temperature falling between -30 and 200°C.

(4) In the invention, the components constituting the catalyst, especially the component (B) may be carried on a

09869331.072601

suitable carrier. For the details of the carrier, the same as in the section of the first aspect shall directly apply also to this section.

II. Method for producing olefinic polymers:

1. Monomers to be polymerized:

In the method of the invention for producing olefinic polymers, used is the above-mentioned catalyst for polymerization of olefins. The catalyst is favorable to homopolymerization of olefins and to copolymerization of olefins with other olefins (that is, copolymerization of different types of olefins).

Olefins for the method are not specifically defined, but preferred are α -olefins having from 2 to 20 carbon atoms. Especially preferred are ethylene and propylene. For further details of the monomers, olefins, the same as in the section of the first aspect shall directly apply also to this section.

In the invention, one or more olefins such as those mentioned above may be (co)polymerized in any desired combination.

2. Polymerization condition:

In the invention, the polymerization catalyst may be subjected to pre-polymerization. For its details, the same as in the section of the first aspect shall directly apply also to this section.

For the details of the method of polymerizing olefins,

the same as in the section of the first aspect shall directly apply also to this section.

The amount of the catalyst to be used in the polymerization method is preferably so controlled that the component (A) may fall generally between 0.1 and 100 μ moles, but preferably between 0.5 and 25 μ moles, in one liter of the solvent used, in view of the polymerization activity and the reactor efficiency.

Regarding the polymerization condition, the pressure may fall generally between normal pressure and 2000 kg/cm²G (196 MPaG). The reaction temperature may fall generally between -50 and 250°C. For controlling the molecular weight of the polymer to be produced, the type and the amount of the catalyst components to be used and the polymerization temperature shall be suitably controlled, or hydrogen may be introduced into the polymerization system.

The invention is described in more detail with reference to the following Examples, which, however, are not intended to restrict the scope of the invention.

[Example II-1]

(1) 0.875 ml of 2 M triisobutylaluminium was added to a toluene solution of 455 mg (1.75 mmols) of triphenylmethanol at -78°C, and stirred at room temperature for 24 hours. The concentration of the component (C) thus formed was 0.1 mols/liter.

09869331-072604
TOP SECRET

(2) 360 ml of toluene, 40 ml of 1-octene, 1.0 ml of a toluene solution of 1.0 M triisobutylaluminum, 0.1 ml of a toluene solution of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate (10 mmols/liter), and 5 ml of the component (C) prepared in the step (1) were put into a 1.6-liter autoclave equipped with a catalyst feeder tube, in that order, and heated up to 70°C. Next, ethylene was introduced into the autoclave to have a pressure of 0.785 MPaG (8 kg/cm²G). Next, 1.0 μmol of (t-butylamido)dimethyl(tetramethyl-η⁵-cyclopentadienyl)silane-titanium dichloride dissolved in 20 ml of toluene was put into the autoclave via the catalyst feeder tube. Ethylene was continuously introduced into the autoclave so as to have all the time the constant pressure of 8.0 kg/cm²G, and polymerized for 60 minutes. Next, methanol was added to this to stop the polymerization. A large amount of methanol was added to this, and the polymer formed was separated through filtration, and then dried at 60°C under reduced pressure for 4 hours. Thus obtained, the ethylene-1-octene copolymer weighed 46.1 g. As measured through GPC, its weight-average molecular weight was 1,270,000 in terms of ethylene, and its molecular weight distribution was 2.46. As measured through ¹H-NMR, the 1-octene content of the copolymer was 18.4 mol%. [Comparative Example II-1]

The same process as in Example II-1 was repeated, except

that the component (C) prepared in the step of Example II-1 (1) was not added to the polymerization system in the step of Example II-1 (2). As a result, herein obtained was 35.3 g of ethylene-1-octene copolymer. As measured through GPC, its weight-average molecular weight was 1,170,000 in terms of ethylene, and its molecular weight distribution was 2.38. As measured through $^1\text{H-NMR}$, the 1-octene content of the copolymer was 16.7 mol%.

[Example II-2]

400 ml of toluene, 1.0 ml of a toluene solution of 1.0 M triisobutylaluminium, 0.1 ml of a toluene solution of tris(pentafluorophenyl)borane (10 mmols/liter), and 5 ml of the component (C) prepared in the step of Example II-1 (1) were put into a 1.6-liter autoclave equipped with a catalyst feeder tube, in that order, and heated up to 70°C. Next, ethylene was introduced into the autoclave to have a pressure of 0.785 MPaG (8 kg/cm²G). Next, 1.0 μmol of (t-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane-titaniumdimethyl dissolved in 20 ml of toluene was put into the autoclave via the catalyst feeder tube. Ethylene was continuously introduced into the autoclave so as to have all the time the constant pressure of 0.785 MPaG (8.0 kg/cm²G), and polymerized for 60 minutes. Next, methanol was added to this to stop the polymerization. A large amount of methanol was added to this, and the polymer formed was

separated through filtration, and then dried at 60°C under reduced pressure for 4 hours. Thus obtained, the ethylene polymer weighed 16.2 g. As measured through GPC, its weight-average molecular weight was 1,140,000 in terms of ethylene, and its molecular weight distribution was 1.98.

[Comparative Example II-2]

The same process as in Example II-2 was repeated, except that the component (C) prepared in the step of Example II-1 (1) was not added to the polymerization system. As a result, herein obtained was 10.5 g of ethylene polymer. As measured through GPC, its weight-average molecular weight was 1,090,000 in terms of ethylene, and its molecular weight distribution was 2.02.

[Example II-3]

The same process as in Example II-2 was repeated, except that pentamethylcyclopentadienyltitanium trimethoxide was used in place of (t-butylamido)dimethyl(tetramethyl- η 5-cyclopentadienyl)silane-titaniumdimethyl. As a result, herein obtained was 5.4 g of ethylene polymer. As measured through GPC, its weight-average molecular weight was 1,090,000 in terms of ethylene, and its molecular weight distribution was 2.02.

[Comparative Example II-3]

The same process as in Example II-3 was repeated, except that the component (C) was not added to the polymerization

system. As a result, herein obtained was 3.7 g of ethylene polymer. As measured through GPC, its weight-average molecular weight was 1,090,000 in terms of ethylene, and its molecular weight distribution was 2.02.

[Example II-4]

(1) Preparation of component (C):

0.875 ml of 2 M triisobutylaluminium was added to a toluene solution of 1.75 mmols of tricyclohexylmethanol (from Across) at -78°C, and stirred at room temperature for 24 hours. The concentration of the component (C) thus formed was 0.1 mols/liter.

Through ¹H-NMR, the product was confirmed to have the component (C) formed therein.

(2) Polymerization of ethylene:

Ethylene was polymerized in the same manner as in Example II-1, except that the compound prepared in the above step (1) was used as the component (C) in place of that prepared in the step of Example II-1 (1). As a result, herein obtained was 8.7 g of ethylene polymer. As measured through GPC, its weight-average molecular weight was 1,100,000 in terms of ethylene, and its molecular weight distribution was 2.05.

[Example II-5]

The same process as in Example II-2 was repeated, except that dimethylsilylenebisbenzoindenylzirconium dichloride was used in place of (t-butylamido)dimethyl(tetramethyl-η⁵-

cyclopentadienyl)silane-titaniumdimethyl, and that propylene was used in place of ethylene. As a result, herein obtained was 34.1 g of propylene polymer. As measured through GPC, its weight-average molecular weight was 1,050,000, and its molecular weight distribution was 2.03.

[Comparative Example II-4]

The same process as in Example II-5 was repeated, except that the component (C) was not added to the polymerization system. As a result, herein obtained was 16.4 g of propylene polymer. As measured through GPC, its weight-average molecular weight was 980,000, and its molecular weight distribution was 2.04.

INDUSTRIAL APPLICABILITY

The catalysts of the invention for polymerization of olefins have the advantages of enhancing the polymerization activity and reducing the amount of the promoter such as oxygen-containing compounds, etc. Using them, therefore, olefinic polymers can be produced efficiently and inexpensively.